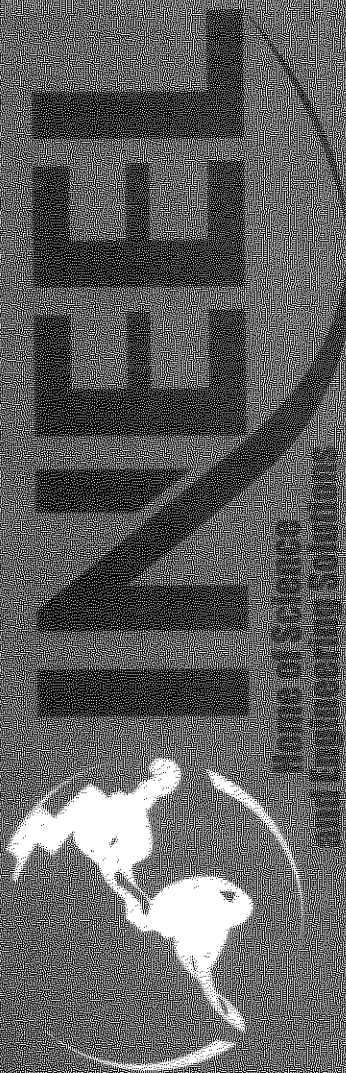


***Cold Bench-Scale
Test Plan for Chemical
Oxidation/Stabilization of
Surrogate V-Tank Waste
(TSF 09/18) at Waste Area
Group 1, Operable Unit 1-10***

July 2003



*Idaho National Engineering and Environmental Laboratory
Bechtel BWXT Idaho, LLC*

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July 2003

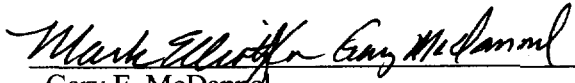
**Idaho National Engineering and Environmental Laboratory
Idaho Completion Project
Idaho Falls, Idaho 83415**

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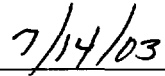
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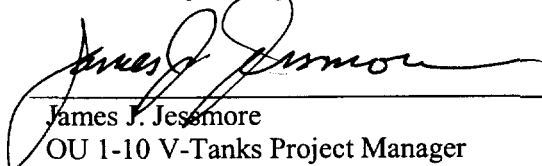
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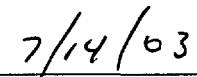
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Date

ABSTRACT

The V-Tanks located at Test Area North, Technical Support Facility 09/18, Waste Area Group 1, Operable Unit 1-10 at the Idaho National Engineering and Environmental Laboratory require treatment for remediation. Each of the four V-Tanks—designated as Tanks V-1, V-2, V-3, and V-9—contains a combination of liquid and sludge that is contaminated with metals, organics, and radionuclides. This report describes cold bench-scale tests that will be performed by MSE Technology Applications, Inc. to confirm the effectiveness of chemical oxidation and grouting in treating the V-Tank contents for disposal. These tests also will determine conditions that minimize the loss of reagents, and the related process parameters such as heat and gas generation that will aid in engineering design of the treatment process.

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ACRONYMS

BBWI	Bechtel BWXT Idaho, LLC
CCV	continuing calibration verification
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFT	contaminant for treatment
COP	chemical oxidation process
CSTR	continued stirred tank reactor
DOE	U.S. Department of Energy
DOE-ID	U.S. Department of Energy Idaho Operations Office
DQO	data quality objective
DRE	destruction and removal efficiency
EPA	U.S. Environmental Protection Agency
ES-CO/S	ex situ chemical oxidation followed by grout stabilization
FY	fiscal year
GC	gas chromatograph
HDPE	high-density polyethylene
ICDF	INEEL CERCLA Disposal Facility
IDL	instrument detection limit
INEEL	Idaho National Engineering and Environmental Laboratory
ISE	ion selective electrode
LDR	land disposal restriction
MDL	method detection limit
MS	mass spectrometer
MSE	MSE Technology Applications, Inc.
MXWTP	Mixed Waste Technology Program
PCB	polychlorinated biphenyl

PCE	perchloroethylene
QA	quality assurance
QC	quality control
RCRA	Resource Conservation and Recovery Act
ROD	Record of Decision
RPD	relative percent difference
RSD	relative standard deviation
SOW	Statement of Work
SVOC	semivolatile organic compound
TAN	Test Area North
TBD	to be determined
TCA	trichloroethane
TCD	thermal conductivity detector
TCE	trichloroethylene
TCLP	toxicity characteristic leaching procedure
TO	test objective
TOC	total organic carbon
TSF	Technical Support Facility
UTS	universal treatment standard
VOA	volatile organic analysis
VOC	volatile organic compound
WAG	waste area group
WETO	Western Environmental Technology Office

Cold Bench-Scale Test Plan for Chemical Oxidation/Stabilization of Surrogate V-Tank Waste (TSF 09/18) at Waste Area Group 1, Operable Unit 1-10

1. INTRODUCTION

Bechtel BWXT Idaho, LLC (BBWI) has begun planning remediation efforts for the V-Tanks at the Idaho National Engineering and Environmental Laboratory (INEEL), Test Area North (TAN), Waste Area Group (WAG) 1, Operable Unit 1-10. Test Area North is one of ten Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) WAGs at the INEEL. Each of the four V-Tanks—designated as Tanks V-1, V-2, V-3, and V-9—contains a combination of liquid and sludge that is contaminated with metals, organics, and radionuclides.

The MSE Technology Applications, Inc. (MSE) is supporting BBWI by performing a cold (i.e., non-radiological) bench-scale study using surrogates of V-Tank waste. The overall goal of the bench-scale tests is to determine the conditions necessary for ex situ chemical oxidation followed by grout stabilization (ES-CO/S) to meet onsite land disposal restrictions (LDRs) for organic and heavy metal contaminants for treatment (CFTs). The ES-CO/S was selected from a list of seven candidate treatment options that were considered. The purpose of the bench-scale cold tests is to determine whether statistically significant destruction of contaminants for treatment (CFTs) can be achieved by ES-CO/S and, if significant, to demonstrate the extent of that destruction and determine the efficiency of each oxidation reaction. This information will be used to determine whether it is reasonable to proceed with planned future laboratory studies on actual V-Tank wastes, and to provide data for supporting title design and future laboratory testing.

A Record of Decision (ROD) amendment will be finalized in Calendar Year 2003. It is anticipated that the ROD will state that ES-CO/S will be the remedy for the V-Tanks' contents, with the INEEL CERCLA Disposal Facility (ICDF) identified as the primary targeted disposal site. Execution of the remedy is expected by the year 2006. This study will determine the performance of ES-CO/S on a surrogate of the tanks' contents, and provide information to assist in the treatment units' process design. The ES-CO/S technology is proven for aqueous systems; however, this technology has not been fully demonstrated for multiphase systems, such as the V-Tank waste.^a The *Laboratory Study Work Plan for Chemical Oxidation and Stabilization of V-Tanks Contents, TSF-09/18, at Waste Area Group 1, Operable Unit 1-10* (DOE-ID 2003) provides expanded details.

Test Objective (TO) 1 of the bench-scale testing is determination of “minimal” to “aggressive” operating conditions “that can reasonably be expected to produce the required results” (see footnote a). Initial studies have identified safe operating conditions for surrogate waste treatment. The CFT destruction associated with these conditions will be evaluated during the bench-scale study outlined in this test plan.

a. MSE Technology Applications, Inc., 2003, “Scoping Phase Test Plan for V-Tank Chemical Oxidation (Draft),” MSE Technology Applications, Inc., May 2003.

1.1 Overview of Chemical Oxidation Technologies

At the project's onset, a literature review pertaining to Fenton's-based oxidation of a wide variety of halogenated organic compounds (including polychlorinated biphenyls [PCBs] and dioxins) in both aqueous and soil/sediment matrices was performed. Based on this effort, it is determined that 50% by weight hydrogen peroxide (H_2O_2) and ferrous sulfate solution initially containing approximately 2 g/L ferrous ion (Fe^{+2}) should be sufficient for treating the given V-Tank surrogate.

1.2 Surrogate Composition

Bechtel BWXT Idaho, LLC, provided MSE with the surrogate formulation to be used in the bench-scale study. The following sections describe the V-Tank waste volume (Table 1), provide characterization data for the V-Tank waste (Table 2), and provide the recipe for the V-tank surrogate (Table 3) to be used during the bench-scale cold study. Averages in Table 2 are included for information only, and do not describe the surrogate composition.

The V-Tanks are four underground tanks that were installed at the TAN Technical Support Facility (TSF) in the early 1950s as part of a system designed to collect and treat radioactive liquid effluents. The purpose of Tanks V-1, V-2, and V-3 (designated as TSF-09) was to store liquid radioactive waste generated at TAN before treatment. Tank V-9 (designated as TSF-18) is a smaller tank of a much different shape than the other three. Its purpose was to act as a clarifier, through gravitation and utilization of its designed shape, for the liquid streams entering Tanks V-1, V-2, or V-3. Waste was pumped to these tanks from the TSF laboratories and craft shops, the hot and warm shops, a radioactive decontamination shop, hot cells, and the Initial Engine Test Facility. In 1968, a large quantity of oil containing PCBs at 680 ppm was discovered in Tank V-2, and the tank was taken out of service subsequently. The oil was removed from Tank V-2 in 1981, and the waste in all three tanks was removed in 1982. The tanks have not been used since the 1980s, although liquid was accidentally discharged to Tank V-3 in the late 1980s. The V-Tank contents were sampled in 1993 and again in 1996.

Because Site TSF-18 (Tank V-9) is contiguous with and received the same waste as TSF-09 (Tanks V-1, V-2, and V-3), the two sites have been combined for characterization and remedial analysis purposes (Richardson et al. 1998). Total volumes of the tank contents are estimated at 1,880 gal of sludge and 10,032 gal of liquid. Table 1 provides the breakdown of the amount for each tank.

Table 1. V-Tank volume data in gallons.

Tank	Capacity	Liquid Volume	Sludge Volume	Total Volume
V-1	10,000	1,164	520	1,684
V-2	10,000	1,138	458	1,596
V-3	10,000	7,660	652	8,312
V-9	400	70	250	320
Total	30,400	10,032	1,880	11,912

Table 2. Data for the contents of the V-Tanks that will be used in this study (DOE-ID 2003).

Component	V-1	V-2	V-3	V-9	Average
Inorganics (mg/kg)					
Aluminum	527	1,120	923	2,690	967
Antimony	5.13	5.35	0.958	11.5	2.44
Arsenic	3.00	3.45	0.860	3.05	1.57
Barium	43.3	38	11.5	299	27.9
Beryllium	8.31	4.24	1.49	20.2	3.36
Cadmium	20.2	22.7	5.09	21.8	10.1
Calcium	1,780	2,240	2,340	6,750	2,420
Chloride	208	102	59.9	397	96.1
Chromium	526	1,120	25.8	1,880	296
Iron	2,630	5,580	5,770	14,600	5,350
Lead	255	303	72.6	454	140
Magnesium	2,640	2,240	3,470	9,010	3,230
Manganese	702	2,230	1,150	4,270	1,500
Mercury	205	116	51.7	1,670	129
Nickel	81.4	76	23.8	319	47.5
Phosphorus	9,630	13,400	15,000	40,400	14,500
Silicon	21,000	22,300	21,900	70,700	24,600
Silver	35.2	50.5	6.95	522	31.7
Zinc	4,460	417	1,340	1,410	1,980
Volatile Organic Compounds (mg/kg)					
PCE	438	138	36.3	425	118
TCA	0.314	0.156	0.044	1770	51.4
TCE	3.85	0.362	0.216	14500	421
Semivolatile Organic Compounds (mg/kg)					
Bis (2-ethylhexyl) phthalate	919	586	338.0	345	453
Polychlorinated biphenyl (Arochlor-1260) or hydrochlorobenzene and biphenyl	34.6	24.4	10.1	95.9	17.9
Radionuclides (nCi/g)					
Cesium	1,740	1,810	527.1	4,480	984.1
Strontium	1,520	3,200	1,499.2	5,180	1,835.3
Transuranic	11	4.02	2.04	26.4	4.27

Note: For selected tests, hydrochlorobenzene and biphenyl may be substituted for Arochlor-1260 to avoid unnecessary costs associated with procuring this reagent. The MSE believes that an inability to effectively destroy these substitutes would serve as a strong indicator that the system could not treat polychlorinated biphenyls. Thus, the use of Arochlor-1260 would be limited to the latter stages of the bench-scale cold tests.

PCE = perchloroethylene.

TCA = trichloroethane.

TCE = trichloroethylene.

Figure 1 illustrates the configuration in which the V-Tanks were operated.

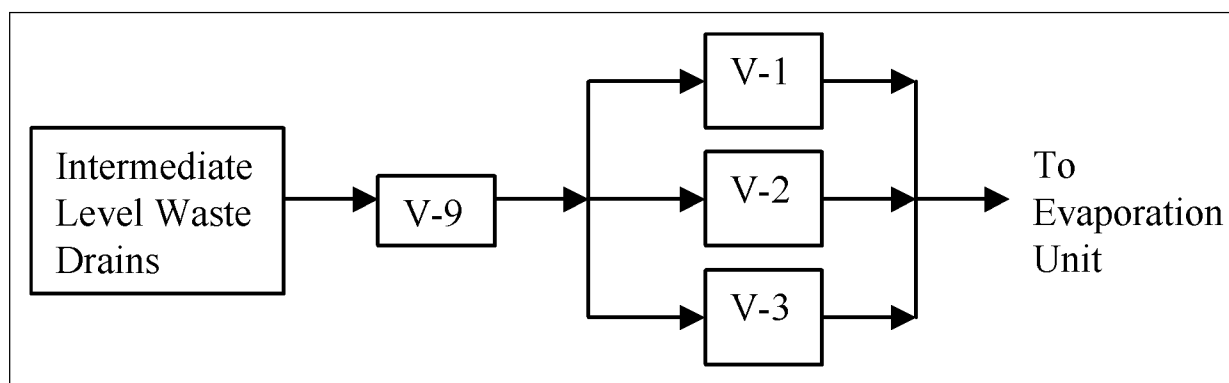


Figure 1. In-use block flow configuration for the V-Tanks.

Waste from operations at TAN-607, TAN-633, and the Initial Engine Test Facility was pumped to Tank V-9 (acting as a solids trap) before disposition into Tank V-1, V-2, or V-3. Liquid was removed from these tanks and sent to an evaporator (i.e., the TAN-616 evaporator, the PM-2A evaporator, or the Idaho Chemical Processing Plant evaporator) (DOE-ID 2003). Table 2 summarizes characterization data for the V-Tanks that were used to develop the surrogate formulation.

The safety analysis performed by the INEEL indicates that the V-Tank waste's radionuclide content makes it necessary to segregate the waste into two streams: (1) combination of Tanks V-1 and V-3 and (2) combination of Tanks V-2 and V-9. Table 3 summarizes the surrogate composition that will be used for the cold bench-scale tests. The INEEL provided the formulation to MSE based on maximum concentrations of each constituent and on historical data for the V-1/V-3 and V-2/V-9 combinations. The maximum concentrations were derived mostly from the V-2/V-9 combination. A total of 6,000 gallons of liquid waste is present in the V-Tanks. A final decision by BBWI has not been made, regarding whether this waste will be decanted before treatment; however, the surrogate was developed assuming that 6,000 gallons of liquid will be removed.

1.3 Overview of Study Design

The starting weights and concentrations (mg/L) of each constituent in the surrogate, surrogate volume and weight, initial pH, temperature conditions, chloride ion concentration, and concentration of gas downstream of the condenser will be known for each experiment. The experimental parameters include temperature (40 or 80°C—starting temperature), amount of oxidizer addition (400 or 500 ml of hydrogen peroxide added during test), and test duration (8 or 12 hours).

System pH will be adjusted initially and then monitored throughout treatment duration at 3.5 ± 0.5 using appropriate additions of concentrated (19 N) sulfuric acid or 4 N sodium hydroxide solutions. The rate of $\text{H}_2\text{O}_2/\text{Fe}^{+2}$ additions will be adjusted so the temperature will increase from approximately 40°C to >80°C initially (via circulating water bath) external temperature control will be applied to maintain temperatures of $\leq 95^\circ\text{C}$ (i.e., not exceeding the slurry's boiling point).

Table 3. Recipe for surrogate formulation.

Component	Weight Percent of Surrogate (%)	Chemical Form	Molecular Weight	Atomic Weight	Grams Used for 10-kg Surrogate Batch
Water	86.0	N/A	N/A	N/A	8,600
Hydraulic oil	1.50	N/A	N/A	N/A	150
Cutting oil	1.50	N/A	N/A	N/A	100
Aluminum	0.127	Al ₂ O ₃	102	27	23.99
Calcium	0.277	CaO	56	40	38.78
Chromium	0.114	Cr ₂ O ₃	152	52	16.66
Iron	0.653	Fe ₂ O ₃	159.7	55.85	93.36
Magnesium	0.314	MgO	40.3	24.3	52.08
Manganese	0.236	MnO	70.93	54.93	30.47
Silicon	2.81	SiO ₂	60.09	28.09	610.1
Phosphorus	1.66	Na ₃ PO ₄	164	31	878.2
Potassium	0.161	KOH	56.1	39.1	23.1
Mercury	0.037	N/A	N/A	N/A	3.7
Arochlor-1260	0.005	N/A	N/A	N/A	0.5
TCE	0.604	N/A	N/A	N/A	60.4
PCE	0.054	N/A	N/A	N/A	5.35
TCA	0.067	N/A	N/A	N/A	6.74
<u>Bis (2-ethylhexyl) phthalate</u>	0.116	N/A	N/A	N/A	11.6

Note: Total weight is above 10,000 g, due to oxygen in inorganic constituents.

PCE = perchloroethylene.

TCA = trichloroethane.

TCE = trichloroethylene.

The following parameters will be monitored:

- pH, temperature, functional group monitoring, and chloride ion,
- Permanent gas analyses (CO₂, CO, O₂, N₂, H₂, and water vapor) in the reactor headspace and condenser receiver outlet periodically throughout the test
- Flow rate of noncondensable gases
- Reaction liquid volume and weight at the end of each experiment
- Concentrations of CFTs at the end of each experiment in the reacted surrogate
- Induction period required

- Weight and chemical analysis of condensate present in the condenser receiver at the end of each experiment.

The pH, temperature readings, chloride ion, and periodic monitoring of organic functional group concentrations will be used to qualitatively assess the time course (and exothermicity) of destruction of the CFTs and/or background oils.

The starting and ending concentrations of CFTs will be used to calculate the experiment-specific destruction and removal efficiency (DRE) for each CFT. Assessment of destruction of background oils during the preliminary phase experiments will provide insight regarding process conditions that may be favorable for chemical oxidation of the V-Tank waste surrogate. During the bench-scale cold tests, these conditions will be replicated and varied slightly to determine the effect of changing selected process variables.

Based upon literature review, MSE suggests that the course of destruction of the background oils and CFTs can be assessed via monitoring the appearance of certain organic functional groups. These functional groups are associated with oxidative degradation of the organic compounds and include alcohols, aldehydes, and carboxylic (fatty) acids. Thus, ml-quantity aliquots of the reaction slurry will be taken hourly during the test runs for the following “spot” analyses:

- Primary and secondary alcohols by chromic anhydride (Jones’s Oxidation)
- Water soluble aldehydes and ketones by basic fuchsin (Schiff’s Reagent)
- Both water soluble and insoluble carboxylic acids by sodium bicarbonate test.

A series of standards of known concentration will be used for each of these tests (i.e., serial dilutions of 37% formalin for aldehydes). This approach will allow semi-quantitative evaluations of changes in concentrations of these functional groups over the course of a given test run.

2. ORGANIZATION AND RESPONSIBILITIES

The V-Tank study’s organization reflects the resources and expertise required for performing the work and producing a technically superior product, while minimizing risks to worker health and safety. The MSE is directly responsible for performing all testing and reporting results to BBWI. The BBWI personnel were responsible for providing the surrogate formulation that best captures the V-Tanks contents’ state.

2.1 Bechtel BWXT Idaho, LLC, Management and Staffing

The BBWI principals involved in this study include the WAG program manager (A. Jantz), the project manager (Jim Jessmore), project engineer (Gary McDannel), principal investigator (E. Miller), and lead engineer (Dale Cresap). Other roles related to the studies are the quality assurance (QA) engineer, regulatory compliance engineer, health and safety engineer, Document Control personnel, and the principal TAN engineer. The project engineer and process engineer from the V-Tanks’ conceptual design study will interface with the study and provide input (such as data quality objectives [DQOs]) for the study. Further information about BBWI’s project organization and responsibilities will be reported in the Laboratory Study Work Plan for Chemical Oxidation and Stabilization of V-Tanks Contents, TSF-09/18, at Waste Area Group 1, Operable Unit 1-10” (DOE-ID 2003).

2.2 MSE Test Personnel

A matrix organizational structure is used by MSE to achieve programmatic objectives. This structure uses existing personnel without duplicating support efforts. A description of personnel assigned to this task is given below:

- **Gene Ashby, U.S. Department of Energy—Western Environmental Technology (WETO) Office Project Officer**—The project officer has the responsibility for the U.S. Department of Energy (DOE) Office of Science and Technology participation in the Mixed Waste Technology Program (MXWTP), reviewing MXWTP final project reports, and providing contractual direction to MSE for the MXWTP.
- **Dan Battleson, Program Manager**—The program manager has the delegated authority to direct all activities and budgets within MSE's MXWTP and is responsible for appointing MSE project managers. The program manager is the main point of contact to the WETO DOE, INEEL DOE, and WAG 1 project manager. The program manager approves change control.
- **Helen Joyce, Project Manager**—The project manager has the delegated authority from the MXWTP program manager to authorize the expenditure of MSE resources to achieve contractual commitments. The project manager defines the work scope, budget, and schedule for the project and submits them for approval to the program manager. The project manager also notifies the program manager of schedule slips, potential cost overruns, and other project variances, with recommended corrective actions. The project manager concurs with the appointment of key project personnel and ensures that all appropriate program/project plans are prepared, reviewed, approved, and implemented by staff assigned to the projects. The project manager is the main point of contact to the BBWI project technical team.
- **Jay Cornish, Technical Lead**—The technical lead is responsible for experimental design, preparation, and review of project documentation. In addition, the technical lead is responsible for analyzing data, determining whether the test objectives have been achieved, and providing recommendations for further testing based on previous results.
- **Steve Kujawa, Ph.D., P.E., Staff Chemical Engineer**—The staff chemical engineer is responsible for design, procurement, setup, and shakedown of test apparatus. In addition, the staff chemical engineer is responsible for preparing project documentation and performing chemical modeling of processes with various test conditions.
- **Clarence Whitworth, Ph.D., Analytical Chemist**—The analytical chemist is responsible for devising the project's sampling and analytical plan, including procurement of analytical services. In addition, the analytical chemist is responsible for reviewing analytical data from MSE and subcontracted laboratories.
- **Jody Bickford, Lead Test Engineer**—The lead test engineer is responsible for executing the tests outlined in this test plan, including the sampling schedule. In addition, the lead test engineer ensures that equipment is procured and calibrated before testing.
- **Michelle Lee, QA Officer**—The QA officer is responsible for reviewing documentation, performing assessments, and submitting QA reports to the program and project managers.

- **Scott Nuthak, Health and Safety Officer**—The health and safety officer is responsible for performing a hazard analysis of the project and documenting the findings in a project-specific Health and Safety Plan.
- **Charles Brown, Environmental Compliance Manager**—The environmental compliance manager is responsible for disposing of experimental residuals in accordance with the appropriate regulations.

2.3 Test Personnel Qualifications

The résumés of MSE test personnel were submitted to the INEEL separately.

3. TEST PLAN OBJECTIVES

As directed by BBWI, the test plan is intended to be flexible in order to allow exploration of reaction conditions to determine effective process conditions, and then vary the oxidation reaction's parameters to find a feasible operating scenario that meets the required DRE objectives. These tests will determine effective process conditions followed by bench-scale parametric tests to better understand and quantify the “most favorable” process.

For this test plan, data quality is defined as screening level. Organic and inorganic CFTs informally identified by BBWI will be the focus of this study (see Table 4). More rigorous analysis and risk assessment activities are currently ongoing to verify that this list of CFTs best represents the compounds expected to drive destruction efficiencies. Table 1 presents the desired destruction efficiencies required for the V-Tanks, taken as a single waste stream, and bringing the organic concentration below the universal treatment standards (UTSs) in the post-oxidation slurry (assuming no volume or weight increase).

Table 4. Maximum organic destruction efficiencies for V-Tanks, taken as a single waste stream.

Organic Contaminant	Total Concentration ^a (mg/kg)	Universal Treatment Standard (mg/kg)	Target Destruction Efficiency (%) if 6,000 gallons of liquid waste is <u>not</u> decanted prior to treatment	Target Destruction Efficiency (%) if 6,000 gallons of liquid waste <u>is</u> decanted prior to treatment
Tetrachloroethylene	118	6	94.9%	97.5%
Trichloroethylene	421	6	98.6%	99.3%
1, 1, 1-Trichloroethane	51.4	6	88.3%	94.3%
Arochlor-1260	17.9	10	44.1%	72.1%
Bis (2-ethylhexyl) phthalate	453	28	93.8%	96.9%

a. The total concentration is based on the averaged contents of all the tanks. Depending on the exact nature of a chosen batch, required destruction efficiencies could differ from those above.

The destruction efficiencies presented in Table 4 assume the following:

- Feed represents a composite of V-Tanks
- No credit is taken for the volume of reagents needed
- No credit is taken for the final cemented waste form
- Arochlor-1260's regulatory limit is for the summation of all Arochlors, so the destruction efficiency implies that final products are not PCBs
- No credit is taken for volatility and escape of volatile organic compounds (VOCs) from the waste mixture during the process of chemical oxidation. Obviously, heating of the reaction mixture without hydrolysis would result in the loss of VOCs because of their volatility. As a result, the necessary destruction of a VOC from chemical oxidation may be much reduced as the VOC is collected in the off-gas system.

Inorganic metal contaminants targeted for treatment by the chemical oxidation/stabilization process include chromium and mercury.

All of the above bullet points except the fourth are conservative. In the actual process, credit will be taken for the items mentioned. Final products of Arochlor-1260 will be determined by analysis.

The reacted products will be stabilized with one or two grout formulations (see Section 8.2) cured at room temperature for 7 days, and subjected to the toxicity characteristic leaching procedure (TCLP) for metals (Cr and Hg). The reacted products will then be cured for 30 days to determine compressive strength of the final waste form and ensure that the solidified final waste form meets the UTS for disposal.

3.1 Test Objectives

The tests will examine aspects of chemical oxidation and stabilization and answer critical questions in order to better define the bench-scale cold tests. The preliminary tests address TO 1 in Statement of Work (SOW) -615, "V-Tank Bench-Scale Test Plan Scope of Work."

TO 1—To determine which of the potential process scenarios are effective in treating surrogated V-Tank waste to regulatory compliance levels, and to identify the most favorable conditions for the chemical oxidation process (COP) scenario for future pilot-scale testing and field deployment. Initial tests should be performed at the extreme ranges of the most aggressive conditions available to us, and at the minimal conditions that can be reasonably expected to produce results. This will establish bounds within which we can refine the effectiveness of the process.

These tests consist of varying surrogate composition, oxidizer input sequence, temperature, rate of oxidizer addition, and amount of oxidizer addition. The results of the initial tests will indicate the "most favorable" conditions that were tested for treatment of V-Tank waste.

Although varying the mixing rate was included in SOW-615 as a variable under TO 1, the experimental setup prevented meaningful experiments for optimizing a mixing rate. Instead, the mixing rate used was not varied and set at the maximum practical rate to ensure homogenization of the flask contents.

MSE has already developed the test plan for the initial phase tests, and tests are ongoing as of this writing (see footnote a on page 1).

3.2 Bench-Scale Cold Test Objectives

The results from tests addressing TO1 will be used to define conditions for the bench-scale cold tests and to address TO 2, TO 3, TO 4, TO 5, TO 7, TO 8, TO 9, and TO 10. Test Objective 6—To estimate changes in leachability between raw waste and oxidized waste—will not be addressed. Test Objective 7—To determine the sequence of destruction—will not be addressed in a rigorous way, but observations will be made to see if the contaminants are destroyed before the oil phase. Tests are planned to determine leachability of inorganic CFTs (Cr and Hg) from final grout stabilized waste forms (see Section 8.2). Some test objectives were edited to better reflect both the actual data to be collected and the conclusions that are possible, based on the current apparatus/experimental design. The bench-scale cold tests have the following objectives:

- TO 2—To determine conversion extent of CFT destruction in the COP. This objective and the following objectives are measurements to be made on both extremes of the process from TO 1, and at a limited number of suitable points in between.
- TO 3—To estimate the rate of heat generation of the COP.
- TO 4—To determine the bulk gas-generation rate of the COP.
- TO 5—To estimate the durability of potential construction materials exposed to the COP.
- TO 7—To determine the sequence and relative extent of destruction.
- TO 8—To propose, and provide data to support, a detailed strategy to prevent autocatalytic reactions for and Fenton's reagent during active remediation.
- TO 9—To determine the behavior of VOCs in the off-gas; volatilization as opposed to destruction.
- TO 10—To determine completion of the destruction of the Resource Conservation and Recovery Act (RCRA) hazardous organics and total organics, and to identify real-time methods for determining completion points.

The bench-scale cold tests described in this test plan have been designed to address the test objectives. As stated above, TO 6—to estimate the changes in leachability between raw waste and oxidized waste for the COP—is no longer being investigated during the bench-scale cold study.

To guide the test sequence, TO 1 has the highest priority, followed by TO 8, then TO 10. These objectives will establish process viability. The remaining TOs are important for defining system parameters.

4. MATERIALS AND METHODS

This section outlines the grade of reagents to be used, describes the test apparatus, and identifies standard methods for sampling and analysis.

4.1 Grade of Reagents

The reagents being used for the bench-scale cold tests are listed in Table 5.

Table 5. Reagents being used for the bench-scale cold tests.

Reagent Name	Grade of Reagent	Comments
Water	Deionized water	—
Hydraulic oil	Technical grade	AW Hydraulic ISO 46
Cutting oil	Technical grade	Cool Tool II
Aluminum oxide (Al_2O_3)	Reagent	—
Calcium oxide (CaO)	Reagent	—
Chromium oxide (Cr_2O_3)	Reagent	—
Iron oxide (Fe_2O_3)	Reagent	—
Magnesium oxide (MgO)	Reagent	—
Manganese oxide (MnO)	Reagent	—
Amorphous silica (SiO_2)	Reagent	—
Sodium phosphate (Na_3PO_4)	Reagent	—
Potassium hydroxide (KOH)	Reagent	—
Mercury	Reagent	—
Arochlor-1260	Reagent	—
Hexachlorobenzene	Reagent	—
Biphenyl	Reagent	—
TCE	Reagent	—
Perchloroethylene	Reagent	—
Trichloroethane	Reagent	—
Bis (2-ethylhexyl) phthalate	Reagent	—
Sulfuric acid	Reagent	—
Sodium hydroxide	Reagent	—
Ferrous sulfate heptahydrate	Reagent	—
H_2O_2 (50%)	Technical	—
Portland Type III (quickset) cement	Technical	—
Portland Type V (acid-resistant) cement	Technical	—
Blast furnace slag	Technical	—
Silica fume	Technical	—
Fly ash	Technical	—

4.2 Test Apparatus Description

The laboratory apparatus to be used for the bench-scale cold tests consists of:

- Three-necked reaction flask connected to a circulating fluid bath (i.e., water for 40°C tests and silicone oil for 80°C tests)
- Reflux condenser with cooling water
- Dewar condenser
- Condensate receiver
- Glass adapters with syringe sampling septum for gas chromatograph (GC) analysis of the off-gas
- Digital and classic bubble meter to measure noncondensable gas generation rate
- Miscellaneous adapters to fit the apparatus together.

Figure 2 illustrates the glassware setup. All equipment is capable of supporting all planned test conditions.

The reaction flask has a nominal volume of 1,000 ml. It is anticipated that the flask's initial reactant volume will be approximately 150 ml of the surrogate mixture; the volume at the end of each experiment will more than double.

The reaction flask is enclosed within an integral glass-water jacket that allows temperature control of its contents with either water or silicone oil. The water or oil used to control the flask's temperature will be pumped from an isothermal water bath. The temperature of the heat transfer fluid will be measured entering and exiting the flask's jacket. The fluid's flow rate will be measured by timing its flow into a graduated cylinder.

Two of the reaction flask's necks will be used to insert electronic probes. A minimum of two probes will measure content temperature and pH. The H_2O_2 concentration, and possibly chloride ion concentration of the reacted products, will be measured after each test. If a suitable probe is found, it will be used for chloride ion. The probe adapters seal the probes with "O" rings.

The reaction flask's central neck will be used to support an adapter that has two necks: the reflux condenser will be inserted into one neck, and peroxide will be fed to the flask through an adaptor on the other neck. The inlet and outlet temperatures of the water that cools the reflux condenser will be measured periodically; the water flow will be measured by timing its rate into a graduated cylinder.

A tee adapter is placed on top of the reflux condenser. The septum adapter is placed on top of the tee to allow syringe sampling of the gas. The tee's other arm is extended to the Dewar condenser's inlet. A spherical joint is used in the middle of the extension to allow easier alignment of the apparatus.

The gas that flows from the reflux condenser will flow into the top of the Dewar condenser. The Dewar condenser will be filled with either an ice-water mixture or possibly an alcohol/dry ice mixture, depending on the desired condensing temperature. Condensate will flow downward into the condenser receiver.

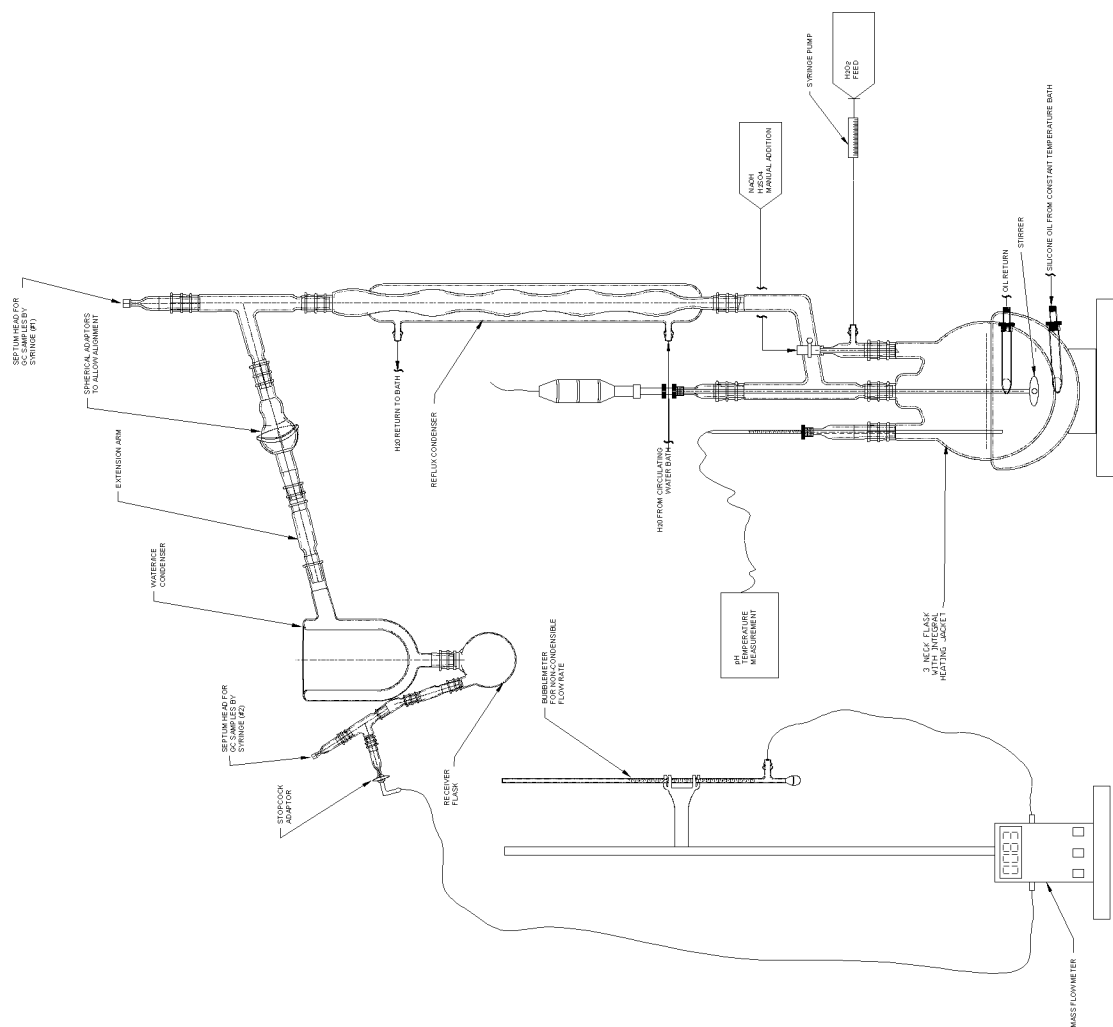


Figure 2. Test apparatus.

The Dewar condenser is a two-necked flask. The gas and condensate flowing into the flask will separate, and the noncondensable gas will flow to an adapter that will allow syringe sampling followed by flow measurement using the bubble meter.

4.3 Standard Methods for Sampling and Analysis

Operating parameters for sampling and/or analysis will include:

- Starting and ending weights/volumes (g/ml) inside the reaction flask using appropriate balances
- Peroxide feed rate(s) in mg/min using a syringe pump (i.e., known flow and H₂O₂ concentration)
- Temperature (°C), pH (standard units), chloride ion using probes or by titration
- Flow rate of noncondensable gases at apparatus outlet, using a bubble meter and digital mass flow meter.

At project onset, samples of emulsion-containing pretreatment and post-treatment levels of CFTs will be sent to BWXT Services of Lynchburg, Virginia. The results will be used to select the laboratory that has the best ability to quantitate the CFTs in the difficult surrogate matrix. Information regarding past analysis of actual V-Tank waste is being gathered to provide insight into extraction and cleanup methods used, as well as other lessons learned.

5. TEST-SCALE STUDY

The objective of reaction-rate testing is to provide empirical process-rate data that will allow correlation of the reaction rate versus reactor conditions for destruction of V-Tank waste using the Fenton's reagent systems.

It is anticipated that the final, scaled-up reactor for waste processing will be a semibatch-stirred tank reactor of the Pfaudler design. An alternative design could include a series of Pfaudler-type reactors with continuous injection of reagent and continuous withdrawal of product slurry. Since the waste is a solids slurry and emulsion system, tubular reactors are most likely ruled out. The V-Tank waste composition is approximated by the components listed in Table 5.

5.1 Reactor Design Equations

As stated above, the scaled-up reactor will probably be semibatch with injection of the oxidizer. A further complication is that the system is primarily aqueous, with initial batch concentrations of oils and CFTs of less than 5 wt%. The complication means that the oil/CFTs must diffuse into the aqueous phase, which could be the rate-controlling step of the process.

Following the *Chemical Engineering Kinetics* (Smith 1970) for a homogeneous, stirred reactor with injection of a reagent, the mass balance for isothermal conditions is (in a relatively superficial example) shown in Equation (1) below:

$$F_0 (W_A)_0 - rV = M_A d(V[A]_1)/dt \quad (1)$$

Where, in our case:

F_0 = the feed rate of the stream containing the reagent

$(w_A)_0$ = the mass fraction of the reagent in the feed stream

r = the reaction rate, a function of at least the concentration of the reagent in the reactor at any time

V = the reactor volume, a function of time

M_A = the mass of the reagent in the reactor at any time

$[A]_1$ = the concentration of the reagent in, and leaving, the reactor at any time (continuous stirred tank reactor [CSTR] definition).

The concentration of the reagent $[A]_1$ in the reactor at any time is related to the above variables by Equation (2):

$$[A]_1 = [(M_A)_i + F_0 (w_A)_0 t] (1 - x) / (M_A V) \quad (2)$$

where:

x = fractional conversion.

Simplifying and stating that there will be no reagent in the reactor at time zero leads to the following expression in Equation (3):

$$(1/t)dt = \left\{ -F_0 (w_A)_0 / (F_0 (w_A)_0 x - Vr) \right\} dx \quad (3)$$

The reactor volume, " V ," and the reaction rate, " r ," are both functions of time. The rate also is a function of conversion, " x ." To solve the equation and determine the concentration of the reactants as a function of time require that " V " and " r " be known for the reacting system, at least empirically, which allows numerical and iterative solution of the differential equation.

The above differential equation illustrates the difficulty of determining a rate expression for " r ," whether empirical or not, when using a semibatch reactor. The rate can be solved for numerically; however, it requires extensive data collection, sample collection, and chemical analyses to obtain a numerical rate. Of course, all of the data are a function of time, and several replications at each operating condition will be needed to determine the variability of the rate as calculated.

According to the literature review, a characteristic of Fenton's oxidation is that they do not necessarily, nor do they probably, convert organic feedstock constituents to the final form of CO_2 , water, and other inorganic forms (mineralization). It will probably be important to identify the reaction products to some extent, especially for permitting purposes.

The reactor mass will contain product concentrations of the oxidizing reagent (probably the most important concentration to know, especially if the reactions are pseudo-first order in the reagent), the reaction intermediates, side reaction products (from calcium and iron reactions), and soluble gases. In theory, most of these concentrations should be known for a complete kinetic study. Because this bench-scale cold study is using batch reactors, certain process conditions cannot be scaled from this study's results. Most of the scalability information for the final process will come from the pilot-scale cold tests performed at MSE in FY 2004.

5.2 Mixing

The bench-scale cold tests will be run in a 1,000-ml glass flask. The effects of mixing on the conversion cannot be determined in such a system—only the gross effects of time, temperature, and

reagent are determined. Therefore, determining an optimum mixing rate cannot be met at this scale. Mixing in the reactor flask will be set at conditions sufficient to ensure practical homogeneity.

The expected results from the flask experiments, since they are not necessarily time constrained, are conversions. These conversions are expected to be near equilibrium for the quantity of oxidizer existing in the reaction mass at steady state during injection, with a tailing off for any extended reaction time beyond the injection period.

Therefore, adequate processing scaling will require evaluation of the effect of mixing on the reactions in a test beyond that proposed in the current plan. The best way to evaluate mixing effects is with a CSTR. In the absence of a CSTR, a semibatch reactor can be used, albeit, with less certainty and ease of analysis.

At least two series of experiments need to be made with stirred reactors configured in the “standard” mode (Figure 3) (see *SME Mineral Processing Handbook* [SME 1985] or *Chemical Process Equipment Selection and Design* [Walas 1990] pg. 288). The mixed reactors should be in the several-liter range and in the tens-of-liter range. The several-liter reactor should be operated at conditions found to be adequate during the definitive series of tests. Process conditions might require reinvestigation, to some extent, to ensure adequate conversion. Then, mixing parameters can be measured.

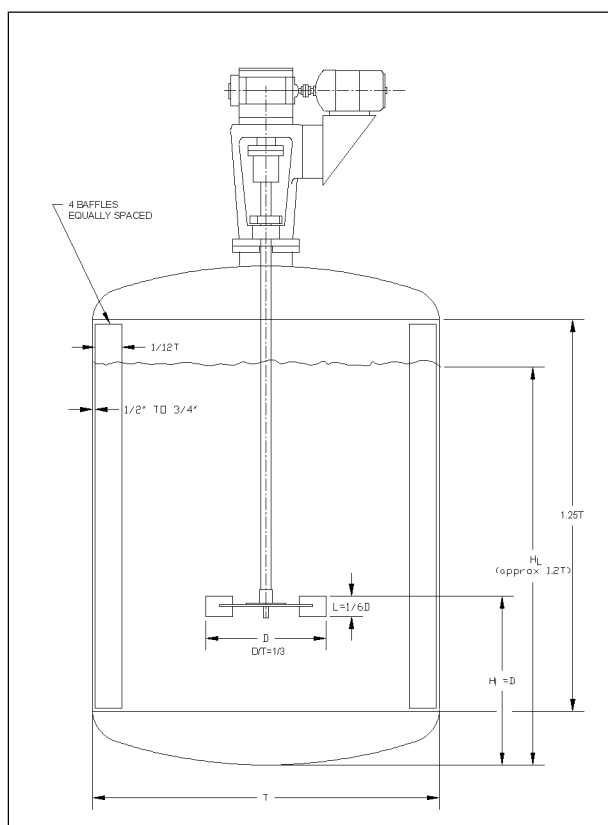


Figure 3. Standard geometry for mixed reactors (SME 1985).

The tens-of-liters reactor then should be operated at the conditions determined at the smaller scale. The results of the tens-of-liters' tests can be used to predict the final reactor size's performance with some confidence, since the process result—conversions—can then be correlated with the mixing dimensionless groups. Heat transfer coefficients for reactor heating and cooling also will be correlated.

Bisio and Kabel (1985) exhaustively illustrate the factors involved in scale up of mixing processes. They suggest that the proper way to scale a chemical reaction mixing process is to:

“Adjust the mixer variables (rotation per minute, impeller diameter, etc.) to achieve the required process result...”

“Quantitatively evaluate the importance of pumping rate and shear rate...”

“Use the quantitative evaluation to predict performance in a larger tank...”

“Test in the larger tank and use the process result as an indicator of critical parameters...”

The authors state that the parameters, power/volume, pumping capacity/volume, impeller tip speed, and Reynolds number are correlating factors for vessels with constant impeller diameter to tank diameter ratio and liquid depth to tank diameter ratio.

To determine the effect on reaction rate versus mixing parameters, the authors suggest that a measurement of the “process result” be used as a dependent variable and the mixer rotation per minute be the first independent variable to be varied. Changing the mixer rotation per minute varies pumping capacity, blending time, and maximum and average shear rates. The process result is plotted against mixer power with rotation per minute as a parameter. A steep slope on the plot indicates a mass transfer-controlled process, usually gas-liquid mass transfer; a zero slope will indicate chemical reaction rate control of the process.

After determining the effect of rotation per minute change, the effect of shear can be determined by varying the impeller diameter to the tank diameter. The effect of increasing impeller diameter is to increase pumping capacity and reduce shear. The authors state that testing at a constant impeller diameter to tank ratio of 0.15 and 0.25 will allow projection of the process result that can be expected from a full-scale reactor with a larger diameter, lower speed impeller (Bisio and Kabel 1985). Finally, performing a limited amount of tests on a larger tank while measuring the process result and noting the change in the various parameters, as well as the power number, will guide the scale up to a larger reactor size.

5.3 Semibatch Scale Up

If the full-scale reactor is to be semibatch, it will need to be designed with sufficient volume to allow for an expected waste volume increase during the course of reaction. The volume increase could be as much as five times, based on reaction stoichiometry. One of the current test program’s main objectives will be to quantify the volume increase.

Once mixing is accounted for and empirical reaction conversions are quantified, the second foreseeable step will be to use the reaction times and conversions to design and pilot the semibatch reactor. The new vessel will need to be designed such that all the mixing parameters will be correct at reactor initiation and near the end of the batch when the mass in the reactor has increased considerably. One result of the increase in reactor mass is that the mixer might have to be of a variable speed design, so the mix time or turnover time can be held relatively constant as the reaction mass increases. It is possible that the bench-scale results imply that a semibatch reactor may not be recommended for the full-scale plant.

6. METHOD VALIDATION TESTING

The test apparatus was designed to ensure proper mass and energy balances, so that data collected will support the achievement of the test objectives. Data collected during the bench-scale tests will allow determination of mass and preliminary energy balances. The overall mass balance closure of each experiment will be determined from the known quantities of the reactants in, and fed to, the reactor flask. The reactor flask contents and the Dewar condenser receiving flask contents will be weighed at the end of the reaction time; noncondensable gas weights will be estimated from the bubble meter flow rates and the GC results estimated at the outlet of the Dewar condenser. Given the current experimental design and the instrumentation uncertainty, it is estimated that these methods will result in accuracy of $\pm 30\%$.

The CFT mass balance will be determined from the known input and analyzed reaction mass concentrations, as well as any gas escaping the system through volatilization. The energy balance will be roughly estimated by measuring the reaction mass temperature and the temperature and flow rates of the reactor flask jacket fluid and condensing mediums over time.

A test will be run with the surrogate composition in the reactor flask, but without addition of oxidizer. The flask contents will be heated to the maximum test temperature (80°C) and allowed to cook for 8 hours. During the tests, measurements planned during the other tests (see Table 7) will be collected during this preliminary test. Upon completion of the test run, the flask contents and condensate will be analyzed for indication that the apparatus is capable of closing the mass balance (particularly the VOCs). This test will provide confidence that the TCE is being destroyed rather than escaping the system through volatilization. This test also will provide an opportunity to shake down the test apparatus and refine real-time monitoring techniques and sampling techniques.

6.1 Hydrogen Peroxide Utilization Efficiency

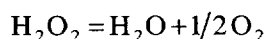
The utilization efficiency is defined as the fraction of peroxide available to be used in the Fenton's reaction divided by the total peroxide fed to the reactor. This fraction can be instantaneous, cumulative to a specific time, or cumulative to the end of the test. The fraction represents the selectivity of the reaction towards oxidation versus oxygen production.

The efficiency will be determined by quantifying the amount of peroxide fed using the syringe pumps versus time, and quantifying the amount of oxygen produced versus time at the exit of the Dewar condenser.

The amount of peroxide fed versus time is measured by the rate of peroxide fed by the syringe pumps to the flask. The total quantity of peroxide delivered at any time is read from the syringe pump controller and is logged. The density of the peroxide solution is used along with its strength to tabulate the total quantity of peroxide fed versus time.

The flowrate of noncondensable gas exiting the Dewar condenser is recorded periodically. The gas flowrate will be corrected for the gas molecular weight and density post-test, once the composition of the gas is available from gas chromatograph results. The instantaneous flow rate of oxygen will then be calculated, using the corrected flowrate and the oxygen concentration from the GC.

Once the rate of oxygen production is calculated, the amount of peroxide that is lost to oxygen can be calculated using the stoichiometry:



The cumulative peroxide efficiency can then be calculated by,

$$\text{Peroxide Efficiency} = 100\% \cdot (\Sigma \text{ Peroxide injected} - 2 \cdot \int \text{ Oxygen rate } d\theta) / (\Sigma \text{ Peroxide injected}) . \quad (4)$$

Equation (4) must be in consistent units. This equation assumes that oxygen is produced only by the above reaction, and leakage of air into the test apparatus is null.

7. IDENTIFYING AND SEQUENCING TEST PARAMETERS (TEST DESIGN)

The initial phase of testing identified safe operating conditions for chemical oxidation of a V-Tank surrogate. The identification and sequencing of test parameters that will be studied during the bench-scale cold tests were defined in SOW-615, "V-Tank Bench-Scale Test Plan Scope of Work." The COP conditions identified during the initial tests represent the point of departure for the bench-scale cold tests outlined in the following sections.

Each run will be one experiment. The primary parameters of each experiment will be the duration of the run, initial reactor temperature, and total amount of oxidizer injected. The results of each experiment will be the final concentration of the CFTs in the reaction products.

The product from each run will have an aqueous phase, possibly an oil phase, and a sludge phase. An attempt will be made to analyze the emulsion for total constituents. If this is not possible, each phase will have to be analyzed separately for the CFT. The weights of each phase and the CFT concentration in each phase will have to be quantified. After chemical analysis, the remainder of each CFT will have to be compared with the quantity in the initial surrogate to determine conversion and, ultimately, the DRE for each CFT. If the analyses provide CFT remainder concentrations in each phase, then an estimate can be made of each contaminant's sequence of destruction.

Since the reactions are most likely diffusion limited, the question of sequence and relative rates of destruction in the aqueous phase (TO 7) is probably irrelevant. Once the reaction is essentially complete, the reaction mass will be quenched or preserved, as appropriate. This quenching will not prevent an unreacted CFT from diffusing into the aqueous phase. Therefore, it is expected that the concentration of contaminant seen in the aqueous phase will be the phase equilibrium concentration.

Autocatalytic reaction is possible, due to the induction period necessary to build up sufficient hydroxide radicals to initiate reaction. During the course of preliminary testing, any autocatalytic reaction should be evident from the results of the experiments. If autocatalytic behavior is observed or the temperature exceeds the test target temperature's boundaries, a slower introduction of the oxidizer might be necessary. If no autocatalytic behavior is observed, experiments will be performed that will gradually increase the rate of addition of oxidizer while observing temperature and violent reaction effects. These data will support TO 8—To propose, and provide data to support, a detailed strategy to prevent autocatalytic reactions for Fenton's reagent during active remediation.

The bench-scale test apparatus will allow syringe sampling of the gas generated during reaction. Gas samples will be taken at the outlet of the reflux condenser and at the outlet of the Dewar condenser. The VOCs of interest are CCl_4 , trichloroethene (C_2HCl_3 , TCE, or trichloroethylene), trichloroethane ($\text{C}_2\text{H}_3\text{Cl}_3$ or TCA), and tetrachloroethene (C_2Cl_4 , PCE, or perchloroethylene). The permanent gases of interest are nitrogen, oxygen, hydrogen, H_2O , CO_2 , and CO.

Noncondensable gas flow rate will be measured by "bubble meter" at the Dewar condenser's outlet to provide data to support TO 4 and TO 9.

To address TO 10—To determine completion of the destruction of the RCRA hazardous organics and total organics—real time data will be correlated to results from each test to identify real-time methods for determining completion points.

The independent variables available for the tests are:

- Feed composition (some tests will use hexachlorobenzene and biphenyl instead of Arochlor-1260)
- Catalyst concentration (will initially mimic effective concentration/doses from initial tests, and may be varied to improve process if necessary)
- Initial temperature (40° or 80°C initial reactor temperature)
- ml of oxidizer fed to the reactor during a given test (400 or 500 ml)
- Duration of test (8 or 12 hours).

The reactor's pH will be controlled to a pH of approximately 3–4 without variation. The temperature can be set at two values for the beginning series of each reaction. For Fenton's, the range will be either 40 or 80°C initial reactor temperature.

Test durations will be 8 or 12 hours. Based on preliminary results, the tests are expected to extend for a time period up to 12 hours; however, the test's durations might have to be adjusted. At the end of each batch test, the reaction will be quenched and the reaction products will be sampled for analysis.

Definitive tests will establish the statistical confidence limits on CFT-specific DREs in complete surrogate slurry, including Arochlor-1260. Test conditions will be set based on the results from previous tests. A one-sided t-test at probability equal to 0.05 will be used to establish the statistical confidence limits on CFT-specific DREs. The planned tests are summarized in Table 6. The procedure developed for the testing is contained in Appendix A.

7.1 Corrosion Tests

The V-Tanks will be used for storing the reaction products after processing, so it is important to know if the final reaction products will adversely affect these materials. To address TO 5—To estimate the durability of potential construction material exposed to the COP—coupons of the V-Tanks' construction materials will be placed in solutions of the expected reaction products that are kept at 20 to 25°C. The tests will determine weight loss of the coupons over time to estimate a corrosion rate for the materials tested. The potential for pitting, crevice corrosion, and stress-corrosion cracking also will be investigated. The corrosion tests will be run for a minimum of 30 days and longer if the schedule permits. The test coupons will apply to the material used for V-Tank fabrication and a material higher and lower in alloy content.

7.2 Grout Stabilization of Reaction Products/Leachability

The MSE's literature review at project onset did not identify any type or composition of grouting agent that was superior to the agent identified in the previous study (Richardson et al. 1998). Thus, MSE evaluated the following grout compositions (in weight percent) during the FY 2002 study (MSE Technology Applications, Inc., 2002a, 2002b):

- E-III mix containing 50% Portland Type III (quickset) cement, 35% blast furnace slag, and 15% silica fume

Table 6. Tests planned for bench-scale cold tests.

Test Sequence	Test Identifier—Purpose	Test Conditions	Surrogate Make-Up	Samples
Prepare samples as soon as contract with BWXT Services is in place.	A-1—Prepare acceptance samples and ship to BWXT	N/A—These samples to be run by BWXT.	Untreated surrogate containing initial levels of VOCs and BEHP; plus untreated surrogate containing practical quantitation limits (PQLs) of VOCs, BEHP, HCB, BP, and Arochlor 1260. Also, include trip blank of DI water only.	VOCs SVOCs PCBs (PQL sample only)
1st	F-1—Shakedown #1 and preliminary estimate of VOC mass balance	T _o =80°C H ₂ O ₂ =0 ml Duration=8 hours O ₂ carrier gas: 20-40 ml/min	TCE, PCE, TCA in DI water	Gas flow/composition; HKM analysis of flask and condensate contents; Chloride ion by ISE
2nd	F-2—Shakedown #2 and refined estimate of VOC mass balance	T _o =40°C H ₂ O ₂ =400 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=8 hours	Full surrogate (organics/metals); substitute HCB/BP for Arochlor 1260	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch
3rd	F-4—Shakedown #4, under even more rigorous treatment conditions	T _o =80°C H ₂ O ₂ =400 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=8 hours	Full surrogate (organics/metals); substitute HCB/BP for Arochlor 1260	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch
4th	F-5—Shakedown #5, under most rigorous conditions presently believed to be safe (105°C maximum operating temperature)	T _o =80°C H ₂ O ₂ =500 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=8 hours	Full surrogate (organics/metals); substitute HCB/BP for Arochlor 1260	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch
Run test as soon as contract with BWXT Services is in place	MV-1—Method validation to verify closure of mass balance	T _o =80°C H ₂ O ₂ =0 ml Duration=8 hours O ₂ carrier gas: 20-40 ml/min	Full surrogate (organics/metals); substitute HCB/BP for Arochlor 1260	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch SVOC/VOC samples sent to BWXT; no Arochlor 1260, therefore no PCB analysis

Table 6. (continued).

Test Sequence	Test Identifier—Purpose	Test Conditions	Surrogate Make-Up	Samples
11th	F-6—Formal replication of test F-3	T _o =40°C H ₂ O ₂ =500 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=8 hours	Full surrogate (organics/metals); substitute HCB/BP for Arochlor 1260	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch; SVOC/VOC samples sent to BWXT; no Arochlor 1260, therefore no PCB analysis
12th	F-7—Formal replication of test F-2	T _o =40°C H ₂ O ₂ =400 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=8 hours	Full surrogate (organics/metals); substitute HCB/BP for Arochlor 1260	Gas flow/composition; HKM analysis condensate contents; Chloride ion by ISE; Run spot tests in batch; SVOC/VOC samples sent to BWXT; no Arochlor 1260; therefore no PCB analysis
5th	F-8—Formal replication of test F-5	T _o =80°C H ₂ O ₂ =500 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=8 hours	Full surrogate (organics/metals); substitute HCB/BP for Arochlor 1260	Gas flow/composition; HKM analysis condensate contents; Chloride ion by ISE; Run spot tests in batch; SVOC/VOC samples sent to BWXT; no Arochlor 1260, therefore no PCB analysis
6th	F-9—Formal replication of test F-4	T _o =80°C H ₂ O ₂ =400 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=8 hours	Full surrogate (organics/metals); substitute HCB/BP for Arochlor 1260	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch; SVOC/VOC samples sent to BWXT; no Arochlor 1260, therefore no PCB analysis
7th	F-10—F-4 test conditions, except for 12-hour treatment time	T _o =80°C H ₂ O ₂ =400 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=12 hours	Full surrogate (organics/metals); substitute HCB/BP for Arochlor 1260	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch; SVOC/VOC samples sent to BWXT; no Arochlor 1260, therefore no PCB analysis

Table 6. (continued).

Test Sequence	Test Identifier—Purpose	Test Conditions	Surrogate Make-Up	Samples
13th	F-11—F-3 test conditions, except for 12-hour treatment time	T _o =40°C H ₂ O ₂ =500 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=12 hours	Full surrogate (organics/metals); substitute HCB/BP for Arochlor 1260	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch; SVOC/VOC samples sent to BWXT; no Arochlor 1260, therefore no PCB analysis
8th	F-12—F-5 test conditions, except for 12-hour total treatment time	T _o =80°C H ₂ O ₂ =500 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=12 hours	Full surrogate (organics/metals); substitute HCB/BP for Arochlor 1260	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch; SVOC/VOC samples sent to BWXT; no Arochlor 1260, therefore no PCB analysis
14th	F-13—F-2 test conditions, except for 12-hour total treatment time	T _o =40°C H ₂ O ₂ =400 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=12 hours	Full surrogate (organics/metals); substitute HCB/BP for Arochlor 1260	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch; SVOC/VOC samples sent to BWXT; no Arochlor 1260, therefore no PCB analysis
9th	F-14—F-10 test conditions, except for surrogate contains Arochlor 1260	T _o =80°C H ₂ O ₂ =400 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=12 hours	Full surrogate (organics/metals), except Arochlor 1260 replaces the HCB/BP	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch; SVOC/VOC samples sent to BWXT, including PCB analysis
15th	F-15—F-13 test conditions, except surrogate contains Arochlor 1260	T _o =40°C H ₂ O ₂ =400 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=12 hours	Full surrogate (organics/metals), except Arochlor 1260 replaces the HCB/BP	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch; SVOC/VOC samples sent to BWXT, including PCB analysis

Table 6. (continued).

Test Sequence	Test Identifier—Purpose	Test Conditions	Surrogate Make-Up	Samples
10th	F-16—F-12 test conditions, except surrogate contains Arochlor 1260	T _o =80°C H ₂ O ₂ =500 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=12 hours	Full surrogate (organics/metals), except Arochlor 1260 replaces the HCB/BP	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch; SVOC/VOC samples sent to BWXT, including PCB analysis
16th	F-17—F-11 test conditions, except surrogate contains Arochlor 1260	T _o =40°C H ₂ O ₂ =500 ml (50 ml in first 10 minutes, then 2 ml/min until total quantity is reached) Duration=12 hours	Full surrogate (organics/metals), except Arochlor 1260 replaces the HCB/BP	Gas flow/composition; HKM analysis of condensate contents; Chloride ion by ISE; Run spot tests in batch; SVOC/VOC samples sent to BWXT, including PCB analysis

- E-V mix containing Type V (acid-resistant) cement, plus the above weight ratios of slag and silica
- B-I mix containing 8% Portland Type I (general purpose) cement, 46% Class C fly ash, and 46% slag
- B-V mix containing Type V cement, plus the above weight ratios of fly ash and slag.

Lafarge North America, Inc., provided the cements, blast furnace slag, and silica fume; ISG Resources provided the Class C fly ash. In all cases, 1.5 g of solid was mixed (dry) into 1 ml of treated slurry. Mixing will be performed manually in the initial work phases.

The TCLP metals (Cr and Hg) results from the previous study at MSE generally indicated that Grout Mix B (fly ash, slag, and cement) could lower mercury to levels complying with the EPA's LDR (i.e., <0.025 mg/L) for this contaminant. This finding is particularly evident for those instances wherein acid-resistant (Type V) cement is used in the formula. Grout Mix E (cement, slag, and silica) appears to be useful, especially if quickset (Type III) cement is incorporated into the mix. Thus, Grout Mix B-V and E-III will be used to stabilize the reaction products from the bench-scale cold tests. The samples will be cured at 25°C for 7 days and subjected to TCLP analysis for mercury and chromium, to ensure that the metals are stabilized to meet UTS disposal requirements. Grouted samples also will be subjected to compressive strength tests and paint filter tests to ensure that no free liquids are present after 30 days cure time.

An enhanced grouting treatment may be performed if prior analyses indicate non-compliance with TCLP standards for Cr and Hg. Two organic sorbents will be investigated: (1) Imbibiter Beads™ IMB230301 (which are composed of spherical alkylstyrene copolymer and kaolin clay particles) that are manufactured by Imbibitive Technologies, Inc., and (2) Petroset II Granular (which is a modified clay granular stabilizing agent) manufactured by Fluid Tech, Inc., that does not require mixing during the waste solidification process. Selected samples will be pretreated with the organic sorbents before grouting. Table 7 summarizes the data collected for chemical oxidation, stabilization, and corrosion tests.

Table 7. Summary of proposed methods for data collection for chemical oxidation/stabilization of V-Tank waste.

Measurement/Observation	Traceability to Test Objectives	Matrix	Sample Frequency	Sample Location	Proposed Method
Measurements for Bench-Scale Cold Tests—Chemical Oxidation					
Weight of reaction flask	TO 2	N/A	Before test	Reaction flask	Balance
Weight of surrogate components	TO 2	Liquid/solid	Before addition to reaction flask	Weighing paper/bottle	Balance
VOCs in surrogate	TO 2	Surrogate emulsion	After surrogate is generated	Surrogate storage container	Gravimetric determination
SVOCs in surrogate	TO 2	Surrogate emulsion	After each batch of surrogate is generated	Surrogate storage container	Gravimetric determination
PCBs in surrogate	TO 2	Surrogate emulsion	After each batch of surrogate is generated	Surrogate storage container	Gravimetric determination
Metals in surrogate	TO 2	Surrogate emulsion	After each batch of surrogate is generated	Surrogate storage container	Gravimetric determination
Mercury in surrogate	TO 2	Surrogate emulsion	After each batch of surrogate is generated	Surrogate storage container	Gravimetric determination
Initial volume of surrogate	TO 2	Surrogate emulsion	Before test	Reaction flask	Graduated cylinder
Initial weight of surrogate	TO 2	Surrogate emulsion	Before test	Reaction flask	Balance
Temperature of fluid bath/temperature of fluid entering flask jacket	TO 3	Liquid	Every 15 minutes during test	Fluid bath readout/thermometer in fluid bath	Thermometer
Temperature of water exiting flask jacket	TO 3	Liquid	Every 15 minutes during test	Exit of flask fluid jacket at return to bath	Thermometer
Flow rate of fluid circulating through jacket	TO 3	Liquid	Before each test	Fluid exiting flask into bath	Graduate cylinder/stopwatch
Temperature of cooling water at reflux condenser inlet	TO 3	Liquid	Every 15 minutes during test	Reflux condenser inlet	Thermometer
Temperature of cooling water at reflux condenser outlet	TO 3	Liquid	Every 15 minutes during test	Reflux condenser outlet	Thermometer
Flow through reflux condenser	TO 3	Liquid	Before each test	Fluid exiting fluid bath	Graduate cylinder/stopwatch
pH in reaction flask	TO 10	Surrogate emulsion	While adding acid to adjust pH, every 5 minutes during test duration, every minute during excursions	Two probes in reaction flask	pH meter
Temperature in reaction flask	TO 10	Surrogate emulsion	While adding acid to adjust pH, every 5 minutes during test duration, every minute during excursions	Two probes in reaction flask	Thermistor in pH meter
Chloride ion	TO 10	Surrogate emulsion	End of test	Reaction flask	ISE for chloride

Table 7. (continued).

Measurement/Observation	Traceability to Test Objectives	Matrix	Sample Frequency	Sample Location	Proposed Method
Oxidizer flow rate	TO 2, TO 7, TO 8	Liquid	Every 15 minutes during test	Syringe pump	Syringe pump readout
Time interval for each oxidizer flow rate change	TO 2, TO 7, TO 8	N/A	Each time oxidizer flow rate changes	Laboratory clock	Difference in time from interval start to finish
Additions of other reagents to reaction flask (pH adjusters/catalysts, etc.)	TO 2	Liquid/solid	Before every addition, determine weight added.	Transfer container	Balance
Noncondensable gas flow rate at outlet of Dewar condenser	TO 4, TO 9	Gas	Every 10 minutes during test	Bubble meter at apparatus outlet	Bubble meters and mass flow meter
Gas at outlet of Dewar condenser	TO 4, TO 9	Gas	Every 10 minutes during test	Bubble meter at apparatus outlet	Thermocouple
Barometric pressure	TO 3	Air	Daily during testing	Laboratory barometer	Barometer
Ambient temperature	TO 3	Air	Daily during testing	Laboratory thermometer	Thermometer
Gas composition	TO 4, TO 9	Gas	Every 15 minutes during test or more frequently, if possible	Septum at outlet of reflux condenser	EPA Method 18 GC/TCD or GC/MS
Noncondensable gas composition	TO 4, TO 9	Gas	Every 15 minutes during test	Septum at outlet of Dewar condenser	EPA Method 18 GC/TCD or GC/MS
Time to complete test	TO 2, TO 7	N/A	Record the time of test start and finish.	Laboratory clock	Difference in time to nearest minute
Final weight of condensate	TO 4, TO 9	Liquid	After test	Condenser receiving flask	Gravimetric determination
Final weight of surrogate reaction products	TO 2, TO 7	Reacted surrogate	After test	Reaction flask contents	Gravimetric determination
Final volume of surrogate reaction products	TO 2, TO 7	Reacted surrogate	After test	Reaction flask contents	Graduated cylinder
VOCs in surrogate reaction products	TO 2, TO 7	Reacted surrogate	After test	Reaction flask	SW-846 8260B
SVOCs in surrogate reaction products	TO 2, TO 7	Reacted surrogate	After test	Reaction flask	SW-846 8270C
PCBs in surrogate reaction products	TO 2, TO 7	Reacted surrogate	After test	Reaction flask	SW-846 8082
Metals in surrogate reaction products	TO 2, TO 7	Reacted surrogate from definitive runs	After test	Reaction flask	SW-846 3050B and 6010B
Mercury in surrogate reaction products	TO 2, TO 7	Reacted surrogate	After test	Reaction flask	SW-846 7470
DRE	TO 2, TO 7, overall objective	N/A	After test	N/A	Calculation from initial and final concentrations of CFTs
Condensate composition	TO 4, TO 9	Condensate	After test	Condenser receiving flask	SW-846 8260B

Table 7. (continued).

Measurement/Observation	Traceability to Test Objectives	Matrix	Sample Frequency	Sample Location	Proposed Method
Weight of reaction flask	TO 2	N/A	After decanting contents of flask	Reaction flask after test	Gravimetric determination
Initial weight of coupon	TO 5	Solid	Measurements for Corrosion Tests Before adding to reaction flask	Material coupons	Gravimetric determination
Final weight of coupon	TO 5	Solid	After corrosion test	Material coupons	Gravimetric determination
Visual inspection/photographing coupons	TO 5	Solid	Before/after corrosion test	Material coupons	Visual
Storage/cure temperature	LDR achievement	Stabilized, reacted surrogate	Daily during cure time	Water bath	Water bath/thermometer
Storage/cure time	LDR achievement	Stabilized, reacted surrogate	Elapsed time for curing	Laboratory clock	Laboratory clock
Ratio of waste to grout	LDR achievement	Stabilized, reacted surrogate	While preparing stabilized, reacted product	Grout mixing container	Gravimetric determination/calculati on
TCLP Metals (Cr and Hg)	UTS for disposal	Stabilized, reacted surrogate	After 7-day cure	Cured grout	SW-846 1311
Paint filter test	ICDF waste acceptance criteria	Stabilized, reacted surrogate from definitive runs	After 30-day cure	Cured grout	SW-846 9095
Compressive strength	ICDF waste acceptance criteria	Stabilized, reacted surrogate from definitive runs	After 30-day cure	Cured grout	Handheld penetrometer
CFT = contaminant for treatment. DO = dissolved oxygen. DRE = destruction and removal efficiency. EPA = U.S. Environmental Protection Agency. GC = gas chromatograph. ICDF = INEEL CERCLA Disposal Facility. ISE = ion selective electrode. LDR = land disposal restriction. MS = mass spectrometer. PCB = polychlorinated biphenyl. SVOC = semivolatile organic compound. TCD = thermal conductivity conductor. TCLP = toxicity characteristic leaching procedure. TO = test objective. UTS = universal treatment standard. VOC = volatile organic compound.					

7.3 Provisions for Modifying Experimental Activities to Meet Test Objectives

The tests described previously specify a set of test conditions and an allowable envelope of conditions for further testing. For tests outside the specified range of conditions, the test plan must be revised and taken through the normal review process before testing under the new conditions. For example, the duration of the tests might need to be extended to ensure adequate DREs. Table 8 shows the sampling requirements for analytical laboratory work.

Table 8. Sampling requirements for analytical laboratory work.

Analytical Parameter	Sampling Requirements
Metals	≤50-ml emulsion placed in 50-ml HDPE bottle and acidified with nitric acid (HNO ₃) to pH <2 and cool to 4°C; 6-month holding time.
PCBs	One 40-ml VOA vial; preservation with 0.008% Na ₂ S ₂ O ₃ ; cool to 4°C; 14 days to extraction and 40 days from extraction to analysis.
Mercury	≤50-ml emulsion placed in 50-ml HDPE bottle and acidified with HNO ₃ to pH <2 and cool to 4°C; 28-day holding time.
VOCs	Two 40-ml VOA vials preserved with ascorbic acid to pH <2 and cooled to 4°C (fill bottles to top with minimal bubbles); 14-day holding time.
SVOCs	One 40-ml VOA vial; preservation with 0.008% Na ₂ S ₂ O ₃ ; cool to 4°C; 7-day holding time.
TCLP Metals (Cr and Hg)	Grouted sample in Ziploc bag; no preservation required; cool to 4°C; 7-day holding time to extraction/40 days after extraction.
Compressive strength	Grouted sample in appropriate mold in Ziploc bag.
HDPE = high-density polyethylene. TCLP = toxicity characteristic leaching procedure. PCB = polychlorinated biphenyl. VOA = volatile organic analysis. SVOC = semivolatile organic compound. VOC = volatile organic compound.	

8. SAFETY AND HEALTH

The bench-scale experiments presented in this test plan will be conducted in the Experimental Shop at the MSE Test Facility.

Before testing, a reaction analysis will be performed to help predict gas generation and temperature rise of the surrogate mixture when the oxidizer is added. Based on this information, a safety envelope will be established and oxidizer feed rates or limits will be identified in this test plan. In addition, the surrogate mixture's temperature will be closely monitored throughout the experiment to avoid an uncontrolled exothermic reaction. Because of the inherent reactive nature of this experiment, certain mixing and testing activities will be conducted in the laboratory hood of the Experimental Shop. Project personnel will receive training on the contents of this test plan, and related material safety data sheets will be reviewed. All material safety data sheets are available in the Experimental Shop. In addition, the experimental apparatus will be leak checked, and all related process vessels and containers will be labeled appropriately in accordance with MSE's Hazard Communication Program. The project health and safety officer will inspect the experimental apparatus before introducing chemicals or gases or energizing electrical

equipment. All work will be conducted in a manner that minimizes personnel risk, and testing shall not be conducted during off-normal work hours without the health and safety officer's approval. In addition, operating test equipment shall not be left unattended for any time other than brief periods (a few minutes).

Experiments will be conducted inside the fume hood with the sash closed. Safety goggles or safety glasses, a laboratory apron, and polyvinyl chloride or polyethylene gloves will be worn when conducting experiments or handling samples under these conditions. Open-toed shoes, tank tops, and shorts are not allowed in the Experimental Shop. In addition, secondary containment trays will be used under the reactor flask and during all chemical-mixing activities. An upgrade in personal protective equipment will be employed during tasks that cannot be conducted with the fume hood sash closed. In such cases, a face shield and chemical-resistant laboratory coat shall be worn in addition to the previously identified glasses/goggles and gloves. Any unusual odors or potential exposures shall be reported immediately to the health and safety officer. The primary and alternate health and safety officers' names are listed below:

- Primary: Scott Nuthak—7440
- Alternate: Rick Obstar—7372.

The reagents used to create the surrogate slurry composition and spent solutions will present both health and physical hazards. These include H_2O_2 at $\geq 35\%$ by weight, strong acids and bases, organochlorine solvents (i.e., TCE and PCE), and probably small quantities of Arochlor-1260. Table 9 lists the published exposure limits, flashpoints, and explosive limits.

This project's key reagent is analytical grade, 35 to 50% by weight H_2O_2 . At these concentrations, H_2O_2 is both a strong oxidizer and corrosive to skin and mucous membranes. When mixed with organic matter at elevated temperatures (especially $\geq 60^\circ\text{C}$), H_2O_2 can rapidly decompose; in these cases, large quantities of heat and gas (water vapor/steam and oxygen) are released. However, considerable care has been taken to avoid these situations. Furthermore, waste treatment experiments will be performed initially at the smallest useful scale (0.1 L) before considering larger volume studies. In addition to the hazards listed herein, numerous surrogate ingredients also are listed as teratogens and mutagens. The test area shall be posted of such, and pregnant women are not allowed in the test area, despite the controls, as a precautionary measure. A means for bonding and grounding will be provided, as well as maintaining surrogate mixtures well below autoignition temperatures, due to the explosive nature of some surrogate ingredients.

Readily available emergency equipment shall include spill-control materials, an emergency eyewash/shower facility, and a 10-lb multipurpose fire extinguisher. Chemical containers shall be stored in an appropriate storage cabinet when not in use. Food and drink shall not be stored in the test refrigerator. Following all work with chemicals or potentially contaminated equipment, personnel shall wash hands immediately before exiting the building and before eating and drinking.

As noted, these experiments will be conducted in the Experimental Shop at the MSE Testing Facility. Eating, drinking, and smoking in the Experimental Shop are prohibited. Good laboratory hygiene and safety practices are required at all times. Good housekeeping and proper chemical storage shall be high priority.

Table 9. Exposure limits, flashpoints, and explosive limits for surrogate compositions.

Compound	Exposure Limit ^a	Flashpoint	Explosive Limits
Trichloroethene	50 ppmv	N/A	8 to 10.5%
Perchloroethene	25 ppmv	N/A	N/A
Arochlor-1260	—	—	—
Hydrochlorobenzene	0.002 mg/m ³	132°C	Not reported
Biphenyl	—	—	—
Elemental mercury	—	—	—
Bis (2-ethylhexyl) phthalate	—	—	—
H ₂ O ₂	1 ppmv	N/A	N/A
Sodium hydroxide	2 mg/m ³	N/A	N/A
Sulfuric acid	1 mg/m ³	N/A	N/A
Portland cement	—	—	—
Hydraulic oil	—	—	—
Cutting oil	—	—	—
Aluminum oxide (Al ₂ O ₃)	—	—	—
Calcium oxide (CaO)	—	—	—
Chromium oxide (Cr ₂ O ₃)	—	—	—
Iron oxide (Fe ₂ O ₃)	—	—	—
Magnesium oxide (MgO)	—	—	—
Manganese oxide (MnO)	—	—	—
Silica (SiO ₂)	—	—	—
Sodium phosphate (Na ₃ PO ₄)	—	—	—
Potassium hydroxide (KOH)	—	—	—
Trichloroethane	—	—	—
Ferrous sulfate heptahydrate	—	—	—
Blast furnace slag	—	—	—
Silica fume	—	—	—
Fly ash	—	—	—
Silica sand	—	—	—

a. Threshold limit value or permissible exposure limit, whichever is lowest.

9. ENVIRONMENTAL/RESIDUALS MANAGEMENT

All waste management activities will be the responsibility of MSE. All waste derived from the bench-scale cold tests will be disposed of according to appropriate regulations.

The Mike Mansfield Advanced Technology Center is registered with the state of Montana as a hazardous waste generator and has an EPA hazardous waste generator identification number issued by the state of Montana. The MSE routinely generates hazardous waste at this facility and manages the waste in accordance with formal operating procedures designed to demonstrate compliance with RCRA and Montana state regulations. The MSE files annual hazardous waste generator and study reports with the state and EPA. Representatives from the Montana State Department of Environmental Quality inspect the facility and facility waste management practices on an annual basis. Formal inspection reports are issued because of these inspections. There are no findings or violations of record.

Waste generated because of this project will be managed by MSE in accordance with facility procedures. Hazardous waste generated as a result of this project will be manifested and disposed of at an RCRA-licensed treatment, storage, and disposal facility, in accordance with all applicable federal and state environmental regulations.

10. QUALITY ASSURANCE/QUALITY CONTROL

Analytical procedures for all instrumentation will follow the quality requirements of referenced methods and the manufacturer's specifications. Generally, these consist of calibrations before, during, and after the analyses and the use of external standards and blanks.

10.1 Bench-Scale Quality Control

Quality control for the bench-scale portion of the experiments will be required for:

- pH measurements
- Temperature readings
- Hydrogen peroxide concentration
- Chloride ion selective electrode (ISE) measurements
- Weight measurements
- Flow measurements
- Gas composition
- Time measurements.

Quality control checks associated with each type of measurement at MSE are discussed in the following sections and are summarized in Table 10.

Table 10. Internal quality control procedures for proposed methods.

Measurement/ Observation	Traceability to Test Objectives		Matrix	Sample Frequency		Sample Location		Method	Accuracy	
Weight of reaction flask	TO 2	N/A		Before test		Reaction flask		Balance	±1%	
Weight of surrogate components	TO 2	Liquid/solid		Before addition to reaction flask		Weighing paper/bottle		Balance	±1%	
VOCs in surrogate (PCE, TCA, TCE)	TO 2	Surrogate emulsion		Before addition to reaction flask		Syringe		Gravimetric determination	±1% for balance—three surrogate batches will be generated and submitted to laboratory for analysis to determine the variance of surrogate generation.	
SVOCs in surrogate (bis [2-ethylhexyl] phthalate, hydrochlorobenzene, biphenyl)	TO 2	Surrogate emulsion		Before addition to reaction flask		Syringe		Gravimetric determination	±1% for balance—three surrogate batches will be generated and submitted to laboratory for analysis to determine the variance of surrogate generation.	
	TO 2	Surrogate emulsion		Before addition to reaction flask		Syringe		Gravimetric determination	±1% for balance—three surrogate batches will be generated and submitted to laboratory for analysis to determine the variance of surrogate generation.	
	TO 2	Surrogate emulsion		Before addition to reaction flask		Weighing paper		Gravimetric determination	±1% for balance—three surrogate batches will be generated and submitted to laboratory for analysis to determine the variance of surrogate generation.	
Mercury in surrogate	TO 2	Surrogate emulsion		Before addition to reaction flask		Syringe		Gravimetric determination	±1% for balance—three surrogate batches will be generated and submitted to laboratory for analysis to determine the variance of surrogate generation.	
Initial volume of surrogate	TO 2	Surrogate emulsion		Before test		Reaction flask		Graduated cylinder	Minor graduations on graduated cylinder	
Initial weight of surrogate	TO 2	Surrogate emulsion		Before test		Reaction flask		Balance	±1%	
Temperature of fluid bath/temperature of fluid entering flask jacket	TO 3	Liquid		Every 15 minutes during test		Fluid bath readout/thermometer in fluid bath		Thermometer	±1°C	
Temperature of water exiting flask jacket	TO 3	Liquid		Every 15 minutes during test		Exit of flask fluid jacket at return to bath		Thermometer	±1°C	
Flow rate of fluid circulating through jacket	TO 3	Liquid		Before each test		Fluid exiting flask into bath		Graduated cylinder/stopwatch	±5%	
Temperature of cooling water at reflux condenser inlet	TO 3	Liquid		Every 15 minutes during test		Reflux condenser inlet		Thermometer	±1°C	
Temperature of cooling water at reflux condenser outlet	TO 3	Liquid		Every 15 minutes during test		Reflux condenser outlet		Thermometer	±1°C	
Flow through reflux condenser	TO 3	Liquid		Before each test		Fluid exiting fluid bath		Graduate cylinder/stopwatch	±5%	
pH in reaction flask	TO 10	Surrogate emulsion		While adding acid to adjust pH, every 5 minutes during test duration, every minute during excursions		One probe in reaction flask		pH meter	±0.05	

Table 10. (continued).

Traceability to Test Objectives		Matrix	Sample Frequency	Sample Location	Method	Accuracy
Measurement/ Observation						
Temperature in reaction flask	TO 10	Surrogate emulsion	While adding acid to adjust pH, every 5 minutes during test duration, every minute during excursions	One probe in reaction flask	Thermistor in pH meter	±1°C
Chloride ion	TO 10	Surrogate emulsion	End of test	Post test	ISE for chloride	±5%
Oxidizer flow rate	TO 2, TO 7, TO 8	Liquid	Every 15 minutes during test	Syringe pump	Syringe pump readout	±0.5%
Time interval for each oxidizer flow rate change	TO 2, TO 7, TO 8	N/A	Each time oxidizer flow rate changes	Laboratory clock	Difference in time from interval start to finish	±5 sec
Additions of other reagents to reaction flask (pH adjusters/catalysts, etc.)	TO 2	Liquid/solid	Before every addition, determine weight added.	Determine average weight of drop and count drops added.	Balance	±1%
Noncondensable gas flow rate at outlet of Dewar condenser	TO 4, TO 9	Gas	Every 10 minutes during test	Bubble meter at apparatus outlet	Bubble meter	±1%
Temperature of gas of outlet of Dewar condenser	TO 4, TO 9	Gas	Every 10 minutes during test	Bubble meter at apparatus outlet	Thermocouple or thermometer	±1°C
Barometric pressure	TO 3	Air	Daily during testing	Laboratory barometer	Barometer in Instrument and Control Shop	±0.1 mm mercury absolute
Ambient temperature	TO 3	Air	Daily during testing	Laboratory thermometer	Thermometer	±1°C
Gas composition	TO 4, TO 9	Gas	Every 15 minutes during test or more frequently if possible	Septum at outlet of reflux condenser	EPA Method 18 GC/TCD or GC/MS	±20% standard recovery
Noncondensable gas composition	TO 4, TO 9	Gas	Every 15 minutes during test	Septum at outlet of Dewar condenser	EPA Method 18 GC/TCD or GC/MS	±20% standard recovery
Time to complete test	TO 2, TO 7	N/A	Record the time of test start and finish.	Laboratory clock	Difference in time to nearest minute	±1 minute
Final weight of condensate	TO 4, TO 9	Liquid	After test	Condenser receiving flask	Gravimetric determination	±1%
Final weight of surrogate reaction products	TO 2, TO 7	Reacted surrogate	After test	Reaction flask contents	Gravimetric determination	±1%
Final volume of surrogate reaction products	TO 2, TO 7	Reacted surrogate	After test	Reaction flask contents	Graduated cylinder	Minor graduations on graduated cylinder
VOCs in surrogate reaction products (PCE, TCA, TCE, other formed)	TO 2, TO 7	Reacted surrogate	After test	Reaction flask	SW-846 8260B	±15% standard recovery
SVOCs in surrogate reaction products (bis [2-ethylhexyl] phthalate, hydrochlorobenzene, biphenyl, others formed)	TO 2, TO 7	Reacted surrogate	After test	Reaction flask	SW-846 8270C	±15% standard recovery
PCBs in surrogate reaction products	TO 2, TO 7	Reacted surrogate	After test	Reaction flask	SW-846 8082	±15% standard recovery
Metals in surrogate reaction products (Al, Ca, Cr, Fe, Mg, Mn, Si, P, K)	TO 2, TO 7	Reacted surrogate	After test	Reaction flask	SW-846 3050B and 6010B	±10% standard recovery
Mercury in surrogate reaction products	TO 2, TO 7	Reacted surrogate	After test	Reaction flask	SW-846 7470	±10% standard recovery
Dissolved organic carbon	TO 2, TO 7	Reacted surrogate	After test	Reaction flask	EPA 415.1	±10% standard recovery

Table 10. (continued).

Measurement/ Observation	Traceability to Test Objectives		Matrix	Sample Frequency	Sample Location	Method	Accuracy
Oil and grease in surrogate reaction products	TO 2, TO 7	Reacted surrogate	After test		Reaction flask	SMWW 5520B	±10% standard recovery
DRE	TO 2, TO 7, overall objective	N/A	After test		N/A	Calculation from initial and final concentrations of CFTs	±15%
Condensate composition	TO 4, TO 9	Condensate	After test		Condenser receiving flask	SW-846 8260B	±15%
Weight of reaction flask	TO 2	N/A	After decanting contents of flask		Reaction flask after test	Gravimetric determination	±1%
Initial weight of coupon	TO 5	Solid	Before adding to reaction flask		Material coupons	Gravimetric determination	±1%
Final weight of coupon	TO 5	Solid	After corrosion test		Material coupons	Gravimetric determination	±1%
Visual inspection/photographing coupons	TO 5	Solid	Before/after corrosion test		Material coupons	Visual	Visual ability
Storage/cure temperature	LDR achievement	Stabilized, reacted surrogate	Daily during cure time		Water bath	Water bath/thermometer	±1°C
Storage/cure time	LDR achievement	Stabilized, reacted surrogate	Elapsed time for curing		Laboratory clock	Laboratory clock	±1 minute
Ratio of waste to grout	LDR achievement	Stabilized, reacted surrogate	While preparing stabilized, reacted product		Grout mixing container	Gravimetric determination/calculation	±1%
TCLP Metals (Cr and Hg)	UTS for disposal	Stabilized, reacted surrogate	After 7-day cure or 30-day cure		Cured grout	SW-846 1311	±25% matrix spike recovery
Paint filter test	ICDF waste acceptance criteria	Stabilized, reacted surrogate	After 30-day cure		Cured grout	SW-846 9095	Pass/fail—visual ability
Compressive strength	ICDF waste acceptance criteria	Stabilized, reacted surrogate	After 30-day cure		Cured grout	Hand-held penetrometer	N/A—precision of duplicate ≤20% relative percent difference
<div>CFT = contaminant for treatment. DRE = destruction and removal efficiency. EPA = U.S. Environmental Protection Agency. GC = gas chromatograph. ICDF = INEEL CERCLA Disposal Facility ISE = ion selective electrode. LDR = land disposal restriction. MS = mass spectrometer. PCB = polychlorinated biphenyl. PCE = perchloroethylene. SVOC = semivolatile organic compound. TCA = trichloroethane. TCD = thermal conductivity detector. TCE = trichloroethylene. TCLP = toxicity characteristic leaching procedure. UTS = universal treatment standard. VOC = volatile organic compound.</div>							

10.1.1 pH Measurements

A pH meter capable of measuring values to ± 0.01 units will be used. The pH probe will be calibrated using two fresh pH-buffer solutions that bracket the expected pH. The meter will be calibrated at the beginning of each test, and calibrations will be documented in the project logbook. The pH buffers will be measured after the test to verify that calibration is still valid. If the pH reading of the calibration verification and the pH of the buffer differ by more than ± 0.1 pH units, then the pH meter will be recalibrated and the pH data from the test will be flagged appropriately.

10.1.2 Temperature Readings

Temperature readings will be documented in liquid matrices. Measurements will be performed using thermometers and thermocouples. Temperature controllers, thermocouples, and thermocouple meters must be calibrated annually. Currently, this equipment has valid calibrations.

10.1.3 Hydrogen Peroxide Concentration

The nominally 48-51% w/w H_2O_2 reagent will be analyzed via titration, with 0.1 molar potassium permanganate solution; the permanganate concentration will be standardized by previous titration with a known quantity of potassium oxalate monohydrate. Replicate analyses of H_2O_2 content will be performed at the time of opening each 500 ml reagent bottle.

10.1.4 Chloride Ion

A chloride ISE, calibrated according to the manufacturer's instructions, will be used to provide near real-time chloride ion concentrations following each test.

10.1.5 Weight Measurements

An analytical balance will be used for weight measurements. Several balances are available at MSE with various capacities and resolution. The balances are calibrated yearly at a National Institute of Standards and Technology-approved secondary standards laboratory, and monthly onsite using a set of calibration weights.

10.1.6 Volume Measurements

Liquid volumes will be measured using volumetric glassware for large volumes (≥ 10 ml) and pipettes and syringes for smaller volumes (< 10 ml). Syringes and pipettes will be calibrated using deionized water and an analytical balance.

10.1.7 Oxidizer Flow Rate

Oxidizer flow rate will be determined using a syringe pump. The syringe pump will be factory calibrated and considered accurate without further calibration.

10.1.8 Noncondensable Gas Flow Rate

The noncondensable gas flow rate will be measured using a mass flow meter and bubble meter. The mass flow meter will be calibrated onsite using various gas mixtures in accordance with manufacturer's instructions. The bubble meter will be factory calibrated and considered accurate without further calibration.

10.1.9 Gas Composition Sampling

Gas composition samples will be collected at two points in the test apparatus. Gaseous aliquots will be collected from the sample ports using gastight syringes. Syringe samples will be analyzed in accordance with the requirements of EPA Method 18, "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography" (EPA 1984), using an Agilent/Hewlett Packard 6890 PLUS GC with a thermal conductivity detector (TCD), or by Agilent/Hewlett Packard 6890 GC coupled to a Hewlett Packard 5972A mass-selective detector. Quality assurance and quality control requirements of Method 18 will be adhered to during the testing. Additional guidance will be obtained from SW-846 Method 8000B, *Determinative Chromatographic Separations* (EPA 1996).

An on-site gas chromatograph/mass spectrometer (GC/MS) will be used to analyze syringe samples for TCE, TCA, and PCE. Before performing analyses, the GC/MS will be calibrated with three standards and a blank, encompassing the concentration range of interest. Only values within the calibration range will be reported.

A blank and midrange-calibration-check sample will be analyzed at the start and end of each analytical run and after every 10 samples. If the measured value of the calibration check is not within 10% of the known value, then the problem will be corrected and any samples not preceded and followed by a valid calibration check will be reanalyzed. If the blank check measured value is greater than 2 ppmV, then the problem will be corrected and any samples not preceded and followed by a valid calibration check will be reanalyzed.

One duplicate sample and one spike analysis will be performed for every 20 samples, whichever is more frequent. Spikes will be 50 to 200% of the sample's measured value. If the difference between the measured values (for a given analyte) for a pair of duplicate samples is greater than 20% of their averaged value, then reported concentrations for that analyte for all samples within the batch of 20 samples (or fraction thereof) will be flagged with a "D." Similarly, if spike recoveries are not within 25% of the known value (for a given analyte), then reported concentrations for all samples within that batch of 20 samples (or fraction thereof) will be flagged with an "S" for that analyte.

An onsite GC/TCD will be used to analyze Tedlar bag samples for hydrogen, nitrogen, oxygen, H₂O, CO₂, and CO. Before performing analyses, the GC/TCD will be calibrated with three standards and a blank, encompassing the concentration range of interest (as predicted by modeling). Only values within the calibration range will be reported.

A blank and midrange-calibration-check sample will be analyzed at the start and end of each analytical run and after every 10 samples. If the measured value of the calibration check is not within 10% of the known value, then the problem will be corrected and any samples not preceded and followed by a valid calibration check will be reanalyzed. If the blank check's measured value is greater than 0.5% (v/v), then the problem will be corrected and any samples not preceded and followed by a valid calibration check will be reanalyzed.

One duplicate sample and one spike analysis will be performed for every 20 samples. Spikes will be 50 to 200% of the sample's measured value for any constituents for which the measured concentration is less than 10% (v/v). If the difference between the measured values (for a given analyte) for a pair of duplicate samples is greater than 20% of their averaged value, then reported concentrations of that analyte for all samples within the batch of 20 samples (or fraction thereof) will be flagged with a "D." Similarly, if spike recoveries are not within 25% of the known value (for a given analyte), then reported concentrations for all samples within that batch of 20 samples (or fraction thereof) will be flagged with an "S," for that analyte.

10.1.10 Time Measurements

Time will be measured using a stopwatch for short time intervals and the laboratory clock for long time intervals. Both time measuring systems will be considered accurate without calibration.

10.2 Analytical Quality Control

Because of problems experienced previously by MSE when analyzing this matrix, BWXT Services of Lynchburg, VA provide organics-related analytical support to this project. It is anticipated that modifications to standard methods, and extraction and cleanup procedures developed previously, will be necessary to achieve the DQOs for this study. Given their experience with actual V-tank waste plus treated waste analyses, BWXT Services are judged most qualified to perform these services.

The list of necessary analyses was developed from the DQOs determined by BBWL. The QC checks associated with each analysis are listed in Table 11.

10.3 Data Handling Quality Control

10.3.1 Logbook Procedures

Personnel conducting the experiments will record test activity in bound notebooks. Data will be logged or recorded on data collection sheets. Each new test day shall be identified by the day and date at the top of the logbook page, and the daily activities will be listed. Each new entry will be designated by a time-of-day entry, and it will start on a new line; data of sufficient detail will be entered to fully describe the activity or data being logged. At the conclusion of each day's activities, the logger will provide their initials at the end of the log for that day and place a diagonal line across the remaining unused page for that day's activities. All entries will be recorded in the logbook or on data collection sheets using waterproof, nonsmearing ink. Calibration data for monitoring/measuring equipment will be recorded, including data. Photographs or digital images will be taken and noted in the logbook for reference. The photos or images will be cataloged and retained for future reference. Each page will be initialed and dated, when filled. Data to be recorded include the measurements and observations identified previously and any other data necessary to reconstruct the experiments for a final report.

10.3.2 Bench-Scale Data Handling

For data generated during the tests at MSE, the test engineer and technician have the primary responsibility for obtaining data of acceptable, known, and documented quality. In order to accomplish this, calibration procedures, duplicate analyses, and independent check standards are documented in the field logbook. Printouts of pH, and chloride ion data also will be stapled into the logbook.

If corrective action is necessary for data that fall outside specified criteria, the test engineer will initiate corrective action at the bench. If corrective action is not possible, the sampler must fully document the reason in the field logbook.

The MSE QA manager is responsible for independent review of field data. Typically, this review is performed during routine data validation activities for a project. Copies of the field logbook are requested from the test team and are reviewed to ensure that calibration and other necessary quality control (QC) checks are being performed, and that sufficient documentation is present. Suspect field data are qualified to alert data users to the limitations of the data. Samplers are notified of any deficiencies and appropriate corrective actions are taken to avoid deficiencies during future data-collection activities.

Table 11. Quality control checks associated with proposed methods.

Proposed Method	Procedure	Frequency	Acceptance Criteria	Corrective Action
VOCs by GC/MS, SW-846 8260B	Calibration	Before project, 5 standard (std) + blank	RSD $\leq 15\%$	Recalibrate the instrument.
	Tune	Every 12 hours	Manufacturer's instructions	Recalibrate the instrument if tune fails
	Continuing calibration verification	Every time instrument is set up, every 12 hours	85 to 115% recovery	Recalibrate the instrument.
	Calibration blank	Following CCV, every 20 samples	<MDL	Recalibrate the instrument.
	System performance check compounds	Every time instrument is set up, every 12 hours	Meet minimum response factors.	Check instrument; recalibrate the instrument.
	Calibration check compounds	Every time instrument is set up, every 12 hours	RPD $\leq 20\%$	Check instrument; recalibrate the instrument.
	Preparation blank	Every 20 samples or each batch, whichever is more frequent	<MDL	Re-preparation, reanalysis of samples
	Matrix spike	Every 20 samples or each batch, whichever is more frequent	70 to 130% recovery	Re-preparation, reanalysis of samples
	Duplicate	Every 20 samples or each batch, whichever is more frequent	70 to 130% recovery	Re-preparation, reanalysis of samples
	Laboratory control sample	Every 20 samples or each batch, whichever is more frequent	70 to 130% recovery	Re-preparation, reanalysis of samples
SVOCs by GC/MS, SW 846 8270C	Calibration	Before project, 5 std + blank	RSD $\leq 15\%$	Recalibrate the instrument.
	Tune	Every 12 hours	Manufacturer's instructions	Recalibrate the instrument if tune fails
	Continuing calibration verification	Every time instrument is set up, every 12 hours	85 to 115% recovery	Recalibrate the instrument.
	Calibration blank	Following CCV, every 20 samples	<MDL	Recalibrate the instrument.
	System performance check compounds	Every time instrument is set up, every 12 hours	Meet minimum response factors.	Check instrument; recalibrate the instrument.
VOCs by GC/MS, SW-846 8260B	Calibration	Before project, 5 standard (std) + blank	RSD $\leq 15\%$	Recalibrate the instrument.
	Tune	Every 12 hours	Manufacturer's instructions	Recalibrate the instrument if tune fails
	Continuing calibration verification	Every time instrument is set up, every 12 hours	85 to 115% recovery	Recalibrate the instrument.
	Calibration blank	Following CCV, every 20 samples	<MDL	Recalibrate the instrument.
	System performance check compounds	Every time instrument is set up, every 12 hours	Meet minimum response factors.	Check instrument; recalibrate the instrument.
	Calibration check compounds	Every time instrument is set up, every 12 hours	RPD $\leq 20\%$	Check instrument; recalibrate the instrument.
	Preparation blank	Every 20 samples or each batch, whichever is more frequent	<MDL	Re-preparation, reanalysis of samples
	Matrix spike	Every 20 samples or each batch, whichever is more frequent	70 to 130% recovery	Re-preparation, reanalysis of samples
	Duplicate	Every 20 samples or each batch, whichever is more frequent	70 to 130% recovery	Re-preparation, reanalysis of samples
	Laboratory control sample	Every 20 samples or each batch, whichever is more frequent	70 to 130% recovery	Re-preparation, reanalysis of samples

Table 11. (continued).

Proposed Method	Procedure	Frequency	Acceptance Criteria	Corrective Action
PCBs by GC, SW-846 8082	Calibration check compounds	Every time instrument is set up, every 12 hours	RPD $\leq 20\%$	Check instrument; recalibrate the instrument.
	Preparation blank	Every 20 samples or each batch, whichever is more frequent	<MDL	Re-preparation, reanalysis of samples
	Matrix spike	Every 20 samples or each batch, whichever is more frequent	70 to 130% recovery	Re-preparation, reanalysis of samples
	Duplicate	Every 20 samples or each batch, whichever is more frequent	70 to 130% recovery	Re-preparation, reanalysis of samples
	Laboratory control sample	Every 20 samples or each batch, whichever is more frequent	70 to 130% recovery	Re-preparation, reanalysis of samples
	Calibration	Before project, 5 std + blank	RSD $\leq 20\%$	Recalibrate the instrument.
	Tune	Every 12 hours	Manufacturer's instructions	Recalibrate the instrument if tune fails
	QC reference sample	Every time instrument is set up, every 12 hours	80 to 120% recovery of certified value	Recalibrate the instrument.
	Continuing calibration verification	Beginning of run, every 10 samples, end of run	85 to 115% recovery	Check instrument; recalibrate the instrument.
	Preparation blank	Every 20 samples or each batch, whichever is more frequent	<MDL	Re-preparation, reanalysis of samples
TCLP Metals (Cr AND Hg), SW-846 1311	Matrix spike	Every 20 samples or each batch, whichever is more frequent	70 to 130% recovery	Re-preparation, reanalysis of samples
	Duplicate	Every 20 samples or each batch, whichever is more frequent	70 to 130% recovery	Re-preparation, reanalysis of associated samples
	Laboratory control sample	Every 20 samples or each batch, whichever is more frequent	70 to 130% recovery	Re-preparation, reanalysis of associated samples
	Extraction blank	Every 20 samples or each batch, whichever is more frequent	≤ 2 times the IDL	Flag the results and evaluate for usability.
	Extraction duplicate	Every 20 samples or each batch, whichever is more frequent	$\leq 20\%$ RPD	Flag the results and evaluate for usability.

Table 11. (continued).

Proposed Method	Procedure	Frequency	Acceptance Criteria	Corrective Action
SW-846 3005 (sample preparation for TCLP)	Extraction spike	Every 20 samples or each batch, whichever is more frequent	75 to 125% recovery	Flag the results and evaluate for usability.
	Preparation blank	Every 20 samples or each batch, whichever is more frequent	≤2 times the IDL	Re-preparation of samples for affected analyte
	Laboratory control samples	Every 20 samples or each batch, whichever is more frequent	80 to 120% recovery	Re-preparation of samples for affected analyte
	Matrix spike	Every 20 samples or each batch, whichever is more frequent	75 to 125% recovery	Reanalyze, flag the results, and analyze for usability.
	Duplicate	Every 20 samples or each batch, whichever is more frequent	≤20% RPD	Reanalyze, flag the results, and analyze for usability.
Metals acid digestion, SW-846 3051	Preparation blank	Every 20 samples or each batch, whichever is more frequent	≤2 times the IDL	Re-preparation of samples for affected analyte
	Laboratory control samples	Every 20 samples or each batch, whichever is more frequent	80 to 120% recovery	Re-preparation of samples for affected analyte
	Matrix spike	Every 20 samples or each batch, whichever is more frequent	75 to 125% recovery	Reanalyze, flag the results, and analyze for usability.
	Duplicate	Every 20 samples or each batch, whichever is more frequent	≤20% RPD	Reanalyze, flag the results, and analyze for usability.
	Calibration	Each time instrument is set up	Correlation coefficient (r)≥0.995	Recalibrate instrument.
Metals by inductively coupled plasma-atomic emissions spectroscopy, SW-846 6010	Continuing calibration verification	Beginning of run, every 10 samples, end of run	90 to 110% recovery of true value	Recalibrate instrument and reanalyze associated samples.
	Continuing calibration blank	Following CCV	≤2 times the IDL	Recalibrate instrument and reanalyze associated samples.
	Interference check Samples A and B	Following continuing calibration blank at the beginning of run, end of run	80 to 120% recovery of true value, no significant blank readings (2 times IDL)	Terminate analysis, correct problem, recalibrate, and rerun samples.
Compressive strength, hand-held penetrometer	Duplicate sample	Every 20 samples or each batch, whichever is more frequent	≤20% RPD	Reanalyze, flag results, and analyze for usability.

Table 11. (continued).

Proposed Method	Procedure	Frequency	Acceptance Criteria	Corrective Action
Free water determination, Duplicate sample SW-846 9095		Every 20 samples or each batch, whichever is more frequent	≤20% RPD	Reanalyze, flag results, and analyze for usability.
TOC, EPA Method 415.1	Calibration	Each time instrument is set up	Manufacturer's recommendations	Recalibrate instrument.
	Continuing calibration verification	Beginning of run, every 15 samples, end of run	90 to 110% recovery of true value	Recalibrate instrument and reanalyze associated samples.
	Continuous calibration blank	Following CCV	≤2 times the IDL	Recalibrate instrument and reanalyze associated samples.
	Spike duplicate	Every 10 samples	75 to 125% recovery	Reanalyze, flag the results, and analyze for usability.
Anions, EPA Method 300.0	Calibration	Each time instrument is set up	r≥0.995	Recalibrate instrument.
	Continuing calibration verification	Beginning of run, every 10 samples, end of run	90 to 110% recovery of true value	Recalibrate instrument and reanalyze associated samples.
	Continuous calibration blank	Following CCV	≤2 times the IDL	Recalibrate instrument and reanalyze associated samples.
	Preparation blank	Batch, every 10 samples, whichever is greater	≤2 times the IDL	Re-preparation, reanalysis of samples
	Analytical duplicate	Batch, every 10 samples, whichever is greater	≤20% RPD	Flag the results and evaluate for usability.
	Spike	Batch, every 20 samples, whichever is greater	75 to 125% recovery	Flag the results and evaluate for usability.
CCV = continuing calibration verification. GC = gas chromatograph. IDL = instrument detection limit. MDL = method detection limit. MS = mass spectrometry. PCB = polychlorinated biphenyl. QC = quality control. RPD = relative percent difference. RSD = relative standard deviation. SVOC = semivolatile organic compound. TCLP = toxicity characteristic leaching procedure. TOC = total organic carbon. VOC = volatile organic compound.				

10.3.3 Analytical Data Handling

The subcontract laboratory analyst has the primary responsibility for generating data of acceptable, known, and documented quality. The process involves reducing instrumental output to concentration values and verifying that all QC results are acceptable when compared to limits outlined in the appropriate analytical method. The laboratory QA/QC officer performs independent checks of the data, while the laboratory manager has the final responsibility for ensuring that the precision, accuracy, completeness, and comparability of the data are known and documented.

Analysis reports for each sample analyzed by the laboratory will be submitted to the MSE project manager. The MSE QA personnel will perform independent data validation according to the *EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review* (EPA 1994) and *EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review* (EPA 1988) using QA/QC summaries supplied by the laboratory. The QA/QC summaries include calibration data and QC sample results for the associated data.

10.4 Data Analysis and Interpretation

After completion of the preliminary design and the laboratory study work plan experimental phase, the data will be summarized, analyzed, and interpreted to determine the validity and performance of the treatment process. One goal will be to determine the quality of the data collected. Designated analytical data will be checked to assess precision, accuracy, and completeness. If the quality objectives are not met, consensus on a path forward will be sought with BBWI management; the operations contractor; DOE-ID; EPA, Region 10; and the Idaho Department of Environmental Quality.

The data will be both qualitative and quantitative. The qualitative data will include photographic records of the equipment setup, surrogate appearance, logbook entries, descriptions, and sketches. The quantitative data will include measurements of the amounts of surrogate and oxidant used, chemical concentration measurements, laboratory analysis, and results. Data of sufficient quality will be obtained from the work plan study to evaluate the effectiveness and implementability for possible pilot-scale testing or actual treatment of V-Tank waste.

Test results will be interpreted in the context of technology effectiveness, implementability, and costs. Project personnel will summarize the raw data and test results in Engineering Design Files at the end of the laboratory tests. The Engineering Design Files will provide the key information needed for complete data analysis and interpretation in this preliminary design and laboratory study.

Two levels of data quality will be used in this study. Data taken for preliminary selection or adjustment of mix parameters (and not to be relied upon in making final ROD decisions) will be taken in the screening mode. This corresponds to Level I data in the EPA classification system. In order to permit a broad range of data to be gathered at reasonable cost, screening data will be collected from typical, single specimens; single-value measurements will be made in accordance with detailed written procedures. Results will be presented on standard report forms used by the specific contractor. Comparisons with values established as test target goals will be made on a pass/fail basis using estimated allowances for data uncertainty bands. This mode will be applied to all tests that deal with preliminary selection or adjustment of parameters and to peripheral data taken in later phases. These data must not be used as a basis for ROD evaluations or future full-scale design applications.

A second level of data quality will be used for data that are gathered directly for ROD-analysis purposes or as a critical element of a full-scale treatment process. Data taken at this quality level will be developed using definitive test methods. This corresponds to Level III data in the EPA classification

system. All specimen preparation activities will be conducted in accordance with detailed written procedures, and all measurements included in the final report will be taken with instruments calibrated to certified standards.

Complete data packages from each phase of the preliminary design and laboratory study will be sent to BBWI upon completion of the laboratory work associated with that phase. In addition to the analytical data collected during the study, data packages also will contain relevant observations of key parameters and unknowns encountered during testing. The subcontractor will perform all tests in accordance with the test plan and approved laboratory procedures. The data resulting from testing and analysis under each phase will be collected and reported to BBWI in its entirety. The subcontractors, in addition to the subject-matter experts, will offer technical interpretation of specific test results. The final decision on selecting the best set of conditions for treatment based on the overall data will be made by BBWI.

10.5 Data Reporting

The final report will follow the format suggested by BBWI (DOE-ID 2003). The report will include a QA section that documents QA/QC activities and results, including:

- All bench-scale data collected during testing and analytical results from all samples. Data judged to be outlier will be included, along with justification for excluding these outliers from further interpretation.
- The QA/QC data will be readily correlated to primary data. It will clearly indicate the limitations of the data and the range of validity of the conclusions. In addition, the final report will include a summary of the original DQOs and a statement regarding whether these objectives were met. A statement of deviations from this test plan also will be included in the final report.

The MSE personnel and appropriate BBWI and DOE-ID representatives will review and approve the report for release.

11. TRACEABILITY MATRIX

Each data point can be traced to a test objective or waste acceptance criteria. Table 7 includes a column for traceability to each test objective.

12. SCHEDULE

A report summarizing the results of the bench-scale cold tests will be completed by mid-September 2003. A schedule for the FY 2003 work associated with this project is presented in Figure 4.

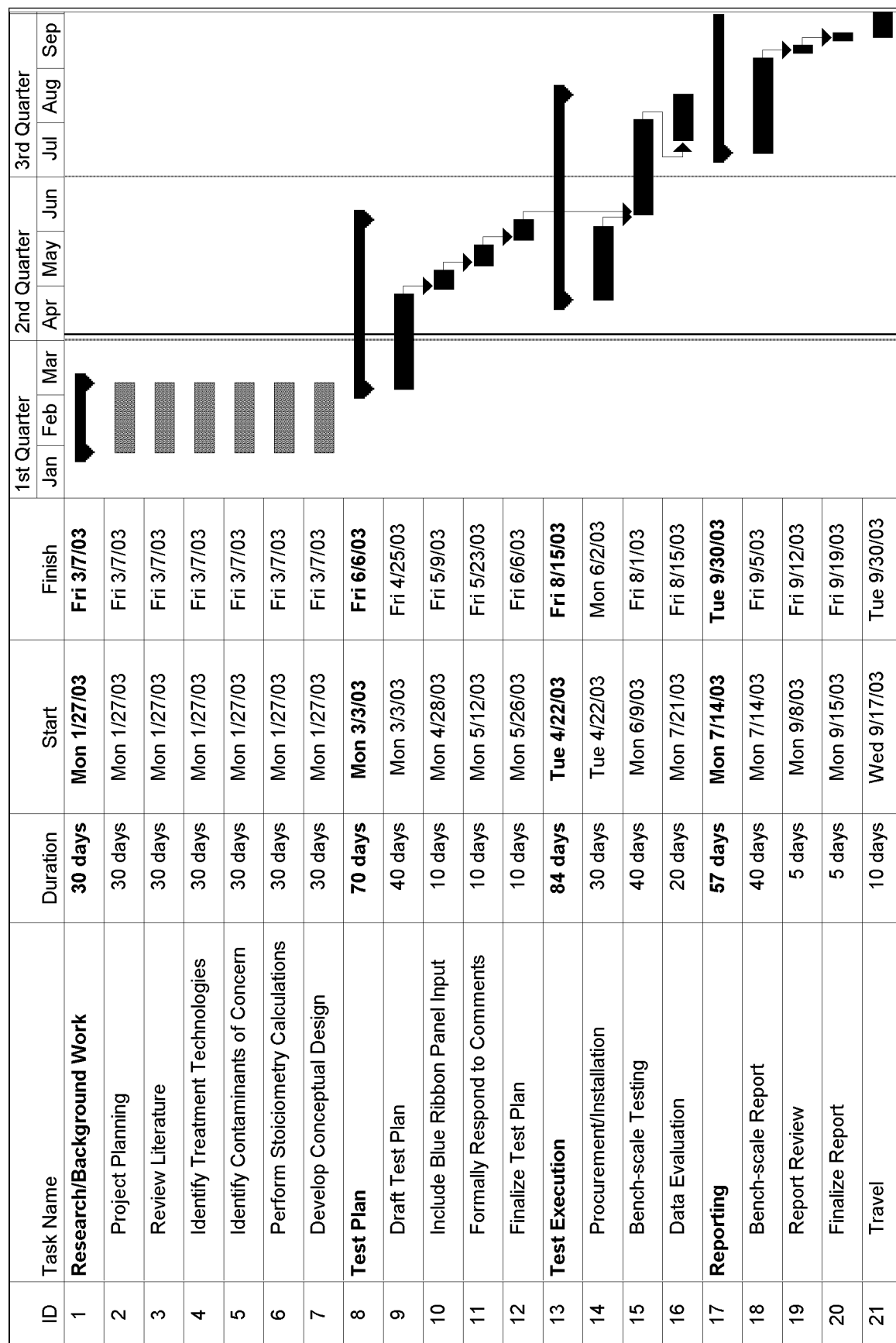


Figure 4. Schedule for the Fiscal Year 2003 work associated with this project.

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